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[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM. NO. 5.]

A STUDY OF THE ZIRCONATES.

BY F. P. VENABLE AND THOMAS CLARKE.

This class of compounds of zirconium has received but little attention from chemists. The chief investigator in the past who has worked in this field was Hiortdahl.¹ Of recent years several papers by L. Ouvrard² have appeared. The accounts given in the various text books of these zirconates are based upon the work of Hiortdahl or upon such abstracts of it as were to be found in the *Jahresberichte*, or in such dictionaries as that of Watts. This is unfortunate, as to the best of our knowledge the work of Hiortdahl itself is in some respects inaccurate and erroneous, and the abstracts of it are misleading. Before giving an account of our own experiments, it may be well to gather together the statements regarding these bodies as given by Watts and in the original article of Hiortdahl.

Watts says that the compounds of zirconia with the stronger bases are obtained by precipitating a zirconium salt with potash or soda, also by igniting zirconia with an alkaline hydroxide. "Zirconate of potassium thus obtained, dissolves completely in water." His first mode of preparing the zirconates is very questionable; the last statement is not true. He then goes on and describes zirconates of sodium, calcium and magnesium, as described by Hiortdahl. The details of Hiortdahl's analyses,

¹ *Ann. Chem. Pharm.*, 137, 34, 236.

² *Compt. Rend.*, 112, 144-46, and 113, 1021-22.

etc., will show on what an imperfect basis the knowledge of the constitution of these bodies rests. Hiortdahl states that he secured direct union only by ignition with alkaline carbonates. His attempts with the volatile chlorides failed. On heating zirconia with sodium carbonate one equivalent of carbon dioxide was driven out, and it is on the loss of carbon dioxide upon ignition that his figures for the composition of the resulting products are largely based. On heating equivalent amounts of zirconia and sodium carbonate a crystalline mass was obtained, which slowly absorbed moisture from the air. On treating this with water no decomposition was noted at first, but soon the water became alkaline and zirconia separated. This was taken as proof that the zirconia was decomposed by the water. In the experiment 0.3910 gram zirconia heated with 0.3130 gram sodium carbonate to a dark redness for nine hours lost 0.1310 gram carbon dioxide, and on treatment with water 0.3871 gram "zirconia," or 99.03 per cent. was left. If an excess of sodium carbonate is used can one drive out two equivalents of carbon dioxide. A little further down he notes that the "Gewichtsverlust zugleich von der Temperatur und der Dauer des Glühens abhängt." These are the determinations from which formulas for the zirconates are worked out.

It is scarcely necessary to say that for purposes of calculation these figures are entirely worthless. The loss of carbon dioxide is due to a partial formation of hydroxide as well as to a combination with zirconia. The fused mass of sodium carbonate, hydroxide, zirconate and unchanged zirconia will of course prove hygroscopic, and water will wash away all except the last two mentioned. We have failed to get any positive evidence that a zirconate formed by fusion was decomposed by water or was appreciably soluble in it.

In his second paper, Hiortdahl treats the fused mass of zirconia and sodium carbonate with water acidified with hydrochloric acid and analyzes the residue, finding in it:

ZrO_3 , 78.54 per cent.; Na_2O , 5.40 per cent.; and H_2O , 16.89 per cent., corresponding to $Na_2O \cdot 8ZrO_3$. He gets zirconate of magnesium and calcium by fusing zirconia and silica with magnesium chloride and calcium chloride respectively.

Ouvrard obtained his zirconates by fusions with the chlorides, also using those of lithium, calcium, strontium and barium. In some cases, instead of using zirconia, he took powdered zircons, obtaining silico-zirconates.

In our own experiments the following methods of forming the zirconates were tried:

I. Fusing in boron trioxide the zirconia and the basic oxide (Ebelmen).

II. Fusing zirconia with alkaline carbonates, (Hiort-dahl).

III. Fusing zirconia with alkaline hydroxides.

IV. Fusing zirconia with alkaline or earthy chlorides (Hiortdahl).

V. Precipitation of solutions of zirconium salts with alkaline hydroxides (Watts).

VI. Dissolving zirconium hydrroxide in strong solutions of sodium or potassium hydroxide and precipitation by dilution or by neutralization with an acid.

I. FUSION WITH BORON TRIOXIDE.

This method, made use of by Ebelmen in the case of other oxides, is useless in the case of zirconia, because this oxide is not taken up by the boron trioxide, and so does not come in contact with the other oxide. The melt of boron trioxide was kept at a high temperature for a number of hours without any appreciable solvent action upon the zirconia, added in small portions.

II. FUSION OF ZIRCONIA WITH ALKALINE CARBONATES.

The purified zirconia used had been dried at the temperature of the steam bath and therefore was not in the inactive condition brought about by igniting it at a very

high temperature. This was the case in the subsequent experiments also.

It is by fusion with sodium carbonate that Hiortdahl claimed to have prepared his zirconates. Ouvrard seems to have gotten little besides crystals of zirconia. Very little action could be seen in the experiments described below. The zirconia sank to the bottom of the fused mass and remained without apparent change for hours. Varying the time of heating did not seem to have much effect upon the results.

After the fused mass had cooled it was leached with successive portions of water until no alkali could be detected. The wash water contained no zirconium. As the mass left will absorb carbon dioxide, it was dried as rapidly as possible at about 150° to constant weight. Dilute hydrochloric acid was used to separate the zirconate formed from the unchanged zirconia. As this zirconia was now in the ignited and even crystalline form, it was concluded that it was insoluble in the dilute acid. The zirconia in the solution was precipitated as hydroxide and determined as oxide, and the alkali determined in the filtrate. Two grams of zirconia were used in each case and a large excess of the carbonate. The amount of unattacked zirconia ranged from ninety-three to ninety-nine per cent., showing thus very little action after many hours of fusion. In some cases, therefore, the amount of supposed zirconate obtained was too small for reliable analysis.

I. WITH SODIUM CARBONATE.

Three experiments with sodium carbonate were carried to completion.

1. Two grams zirconia and eight grams sodium carbonate were fused three hours. Amount of residue after leaching, soluble in dilute hydrochloric acid, 0.1588 gram, or eight per cent. In this $ZrO_2=75.70$ per cent.; $Na_2O=24.30$.

2. Two grams zirconia fused with sixteen grams sodium carbonate for four hours. Amount of residue soluble in hydrochloric acid, 0.3042 grams. Percentages: ZrO_2 , 74.18; Na_2O , 25.81. These correspond fairly with $(\text{ZrO}_2)_3(\text{Na}_2\text{O})_2$.

3. Two grams zirconia fused with sixteen grams sodium carbonate for eight hours. Amount soluble in dilute hydrochloric acid 0.1220 gram, or six per cent. Percentages: ZrO_2 , 58.16; Na_2O , 41.84.

II. WITH POTASSIUM CARBONATE.

When potassium carbonate was used the action was so slight that it was not possible to get enough for analysis. In one case, after heating for ten hours, the amount soluble was just one-half per cent. This accords with the observation of Ouvrard.

Of course it is possible that the leaching with water had a partially decomposing effect upon the zirconates. Very little could be justly concluded, however, from experiments in which there was so little action, therefore the effort at forming the zirconates by fusion with the carbonates was abandoned.

III. FUSION OF ZIRCONIA WITH HYDROXIDES.

1. Fusion with sodium hydroxide.

Here considerable action was noticed. The fusions were made in a silver dish. The heating was kept up until the mass became semi-solid. The treatment of the fused mass and the analysis were carried out as before. No zirconium was detected in the wash water.

1. Two grams zirconia fused with eight grams sodium hydroxide. Total amount dissolved, 1.1855 grams. An analysis, reduced to dry basis, gave ZrO_2 , 92.29, and Na_2O , 7.65.

2. Same amount taken as in experiment 1. Total amount dissolved 0.7655 gram, containing ZrO_2 , 93.19, and Na_2O , 6.22.

3. Two grams zirconia and sixteen grams sodium hydroxide. Amount dissolved 0.8004 gram, containing ZrO_2 , 92.57, and Na_2O , 7.38.

4. Two grams zirconia were fused with eight grams of sodium dioxide, instead of the hydroxide. Amount dissolved 0.7074 gram, and this contained 91.21 per cent. ZrO_2 .

$Na_2O \cdot (ZrO_2)_6$ contains ZrO_2 , 29.30; and NaF_2 , 7.80.

$Na_2O \cdot (ZrO_2)_7$ contains ZrO_2 , 93.29; and Na_2O , 6.79.

2. *Fusion with potassium hydroxide.*

These were carried out in a manner similar to those with sodium hydroxide and the action seemed to be about the same. In each experiment two grams of zirconia were taken and fused with sixteen grams of potassium hydroxide.

1. Dissolved by hydrochloric acid 0.8850 gram which contained 79.63 per cent. ZrO_2 ,

2. Dissolved 1.5241 grams which contained ZrO_2 , 82.98; K_2O , 17.00.

3. Dissolved 1.2078 grams which contained ZrO_2 , 78.59; K_2O , 21.40.

4. Dissolved 0.9297 gram which contained ZrO_2 , 85.51; K_2O , 14.49.

In analyzing these alkaline zirconates the water present was not determined. The moist powder was treated with hydrochloric acid, the insoluble portion caught upon a filter, and the zirconia and alkali determined in the filtrate and the results calculated upon a dry basis. If the analysis given by Hiortdahl is calculated upon a dry basis, it gives for ZrO_2 93.51, and Na_2O , 6.49, or very nearly the numbers gotten in experiment 2 in the fusions with sodium hydroxide.

It is difficult to interpret the results of these fusions with the alkaline carbonates and hydroxides. The fusions do not yield the same definite results each time, and indeed it cannot be claimed from the analyses that definite zirconates have been prepared. Some allowance must be

made for the imperfect method of separation of the zirconate from the unchanged zirconia, some of the former being taken up by prolonged digestion with hydrochloric acid. There is a marked tendency, however, toward the formation of certain zirconates under approximately the same conditions. Two of the experiments with sodium carbonate give results fairly in accordance with the formula $(\text{Na}_2\text{O})_2(\text{ZrO}_2)_3$. In the fusion with sodium hydroxide the results range from $(\text{Na}_2\text{O})(\text{ZrO}_2)_5$ [$\text{ZrO}_2=90.76$; $\text{Na}_2\text{O}=9.24$], to $(\text{Na}_2\text{O})(\text{ZrO}_2)_8$ [$\text{ZrO}_2=94.08$; $\text{Na}_2\text{O}=5.92$], and it is with these that the analysis of Hiortdahl agrees, though his was a fusion with sodium carbonate. Why there should be this difference is not clear. The tendency is manifestly toward the formation of what may be called the polyzirconates, having a considerable excess of zirconic acid. In the case of potassium the carbonate failed to give a compound. The hydroxide gives results ranging from

$(\text{K}_2\text{O})(\text{ZrO}_2)_3$ [$\text{ZrO}_2=79.57$; $\text{K}_2\text{O}=20.43$], to $(\text{ZrO}_2)_5(\text{K}_2\text{O})$, [$\text{ZrO}_2=86.74$; $\text{K}_2\text{O}=13.26$]; again polyzirconates with excess of zirconia.

Other fusions were carried out with sodium and potassium hydroxides, and the resulting masses were leached with dilute acetic acid, a solvent which had to be used in leaching away the alkaline earths in the subsequent experiments. In the case of sodium the leaching removed practically all of the alkali. In the case of potassium a substance containing ZrO_2 , 78.59 per cent., and K_2O , 21.41 per cent. was left. This nearly corresponds to the formula $\text{K}_2\text{O}(\text{ZrO}_2)_3$. It is almost exactly the result gotten in one of the previous experiments.

3. Lithium gave no zirconate when the carbonate was used for the fusion. With the hydroxide it gave the following results:

Two grams ZrO_2 were fused with excess of lithium hydroxide, leached with dilute acetic acid and with water. This gave on analysis ZrO_2 , 89.11 per cent.; Li_2O , 10.99

per cent. Percentage of ZrO_2 calculated for $Li_2O \cdot 2ZrO_2$ is 89.13.

4. Calcium oxide was also heated for a number of hours with zirconia and gave the following results:

	I.	II.	Calculated for $CaO \cdot ZrO_2$.
ZrO_2	70.11	70.83	68.54
CaO	29.88	29.14	31.16

These residues, after treatment with dilute acetic acid and water, were crystalline.

5. Barium hydroxide differs from that of calcium in that it fuses readily and thus affords much better opportunity for reaction. The fusion gave abundant evidence of action. The excess of hydroxide was washed out with water. The carbonate present was dissolved away with dilute acetic acid until there was no more barium in the wash water. No zirconia was found in any of these washings. Towards the latter part of the washing the solid particles settled out with great difficulty. The residue was analyzed with the following result:

	Found.	Calculated for $BaO \cdot ZrO_2$
ZrO_2	55.51	55.95
BaO	44.49	44.05

This is a grayish white powder, very fine and easily soluble in hydrochloric acid. Practically all of the zirconia was taken up, leaving little undissolved by the hydrochloric acid.

6. Strontium oxide was prepared by ignition of the nitrate and heated in the same way as the calcium oxide. This mass was pinkish white, probably from slight impurities, and was completely soluble in dilute hydrochloric acid. On analysis the following results were obtained:

	Found.	Calculated for $SrO \cdot ZrO_2$
ZrO_2	54.22	54.55
SrO	45.77	45.45

7. The magnesia (eight grams) and zirconia (two grams)

was heated together for about four hours and then treated in the same manner as the calcium fusion, *i.e.*, first leached with dilute acetic acid and then washed with water until free from magnesia. The residue gave evidence of being crystalline.

	Found	Calculated for $MgO \cdot ZrO_2$
ZrO_2	76.28	75.30
MgO	23.70	24.70

IV. FUSION OF ZIRCONIA WITH CHLORIDES.

This method was used by Hiortdahl in preparing the zirconates of magnesium and calcium, and by Ouvrard for the same, and also for strontium, barium and lithium. According to the latter they all gave zirconates of the form M_2ZrO_3 .

1. *Fusion with sodium chloride.*

There appeared to be very little action. The fusion was washed with water until free from chlorine. It was then treated as in the case of the carbonates. When two grams of zirconia were fused with sixteen grams of sodium chloride, it was found that less than two per cent. had been dissolved. In a second experiment, after heating six hours, the amount dissolved was less than two-tenths of a per cent.

2. *Fusion with potassium chloride.*

No action was observable. When two grams of zirconia were heated a number of hours with an excess of potassium chloride and the mass then treated as above, only three-tenths of a gram had been acted upon. There seemed to be even less action in the case of lithium chloride at the temperature attainable by means of an ordinary water-blast lamp.

3. *Fusion with alkaline earths.*

Two attempts were made to prepare magnesium zirconate by fusing zirconia with magnesium chloride and ammonium chloride. It was not possible to prevent

decomposition of the magnesium chloride. There seemed to be some action, but much difficulty was experienced in separating the products. The method described by Ouvrard gave evidences of zirconium in the washings.

In the case of fusions with calcium chloride no action could be observed. Two experiments were made, following closely the directions of Ouvrard, except as to temperature possibly, as to which no exact directions were given. A water-blast lamp was used for several hours. After leaching and washing, the mass left behind gave no zirconium to hydrochloric acid.

Our experiments with the chlorides have led us to believe that there is little or no action between zirconia and the chlorides of the alkalies or alkaline earths except where these chlorides are decomposed by the heat and oxides formed. Any action noticed is to be attributed to the oxides.

V. PRECIPITATION FROM THE SOLUTION OF A ZIRCONIUM SALT BY MEANS OF AN ALKALINE HYDROXIDE.

Watts speaks of this method but no experiments are recorded. It seemed to us upon examination of the question that very little evidence as to the existence of the zirconates or their properties could be drawn from such a method of preparation as this. It has been repeatedly observed that the precipitate formed by means of ammonium hydroxide is extremely hard to wash free from ammonia. After a very large number of washings, however, it is practically free from ammonia. The same is true of sodium and potassium hydroxides. Is it to be inferred that a definite zirconate is precipitated? At what point shall the washing be stopped, for manifestly some washing is necessary? Equally, it cannot be decided because of this loss of alkali by prolonged washing, that we have a decomposition of the zirconate caused by the action of the water. It, therefore, seems to be quite useless to make analyses of the precipitates gotten with different degrees

of washing; especially as somewhat similar experiments were carried out under the next heading.

VI. THE SOLUTION OF ZIRCONIUM HYDROXIDE IN CAUSTIC ALKALI.

It was found that zirconium hydroxide was perceptibly soluble in solutions of potassium and sodium hydroxide. Experiments were first made with a view of determining the extent of this solubility. Solutions of the two alkalies were made up of different strengths, an excess of zirconium hydroxide added, and the solution then boiled. After cooling, a measured quantity of the solution was drawn off and the amount of zirconia present determined.

A 50 per cent solution potassium hydroxide dissolved per cc 0.00233 gm.

33 "	"	"	"	"	"	"	"	0.00097	"
25 "	"	"	"	"	"	"	"	0.00075	"
12 "	"	"	"	"	"	"	"	0.00009	"

In the case of sodium hydroxide there seemed to be a stronger solvent action.

A 33 per cent solution dissolves per cc. 0.00245 gram.

25 "	"	"	"	"	"	0.0012	"
12 "	"	"	"	"	"	0.0005	"

If a concentrated solution of alkali, saturated with zirconium hydroxide, is diluted, a portion of the zirconium will be precipitated. Neutralization with acid will also cause a precipitation of the zirconium. In both cases alkali is retained by the precipitate in spite of washing. Analyses were made of some of these precipitates after very thorough washing (in no case was less than a liter of water used.) The results in four experiments were sufficient to show that these precipitates were practically zirconium hydroxides with a varying percentage of alkali, this percentage ranging from 1.15 to 3.94. It is possible to assume that zirconates were formed and then decomposed by the action of water during the washing, but it seems more probable that this is, as is true in the

case of so many hydroxides precipitated by alkaline hydroxides, merely a stubborn retention of alkali. Assuming that the strong alkaline solutions held zirconates in solution, attempts were next made to prepare other zirconates by precipitation from them.

The addition of solutions of various salts gave small precipitates which seemed to be formed mainly because of the dilution of the alkaline hydroxide and to consist almost entirely of zirconium hydroxide. It was necessary, therefore, to use strongly alkaline solutions of the compounds of the elements to be experimented with. This greatly diminished the choice of compounds. Concentrated solutions of aluminum and zinc hydroxides in potassium hydroxide gave precipitates but they were in too small amounts for reliable analyses to be made.

Summing up the results of the experiments performed, it is clear that the method yielding the best results for the preparation of the zirconates is fusion of gently dried zirconia with hydroxides or prolonged heating with the oxides. In the case of the alkaline earths this yields zirconates containing one equivalent of each oxide, $\text{CaO} \cdot \text{ZrO}_2$, etc. The same is true of the magnesium compound. For lithium the compound obtained was $\text{LiO} \cdot \text{ZrO}_2$. For the alkalies it seemed to be possible to obtain only zirconates having a largely preponderating proportion of zirconia. There seems to be a tendency toward the formation of distinct compounds under certain conditions. These polyzirconates, and the lithium compound also, may be decomposition products due to the action of the water used in leaching. No other mode of separation from the products of the fusion could be devised by us, however. If they are produced by the decomposing and solvent action of water, it is a little strange that a point should be reached beyond which the leaching extracted no more alkali, and that this point varied with changed conditions. This is not the case where zirconium hydroxide has been precipitated by an alkali.

DOUBLE ZIRCONATES.

Two attempts at the formation of double zirconates were made.

1. Potassium calcium zirconate.

About two grams each of zirconia, potassium hydroxide and lime were heated together for about four hours. There was evidence of considerable action. The mass was treated with dilute acetic acid and thoroughly washed. Then on treatment with dilute hydrochloric acid nearly the whole residue went into solution. The analysis gave ZrO_2 , 67.21 per cent.; CaO , 31.06; K_2O , 1.11. This is a calcium zirconate, $(CaO.ZrO_2)$, with a small part of the CaO substituted by K_2O .

2. Potassium aluminum zirconate.

Two grams of zirconia were fused for eight hours with two grams potassium hydroxide and three grams of alumina. The mass was washed with dilute acetic acid until no more alumina was dissolved. The residue was treated with dilute hydrochloric acid and the insoluble portion removed by filtration. The analysis gave ZrO_2 , 72.38 per cent; Al_2O_3 , 7.66; K_2O , 20.00. These experiments indicate the possible existence of double zirconates, and when time permits this point will be further examined.

RIVER ADJUSTMENTS IN NORTH CAROLINA.

W. J. WEAVER.

NOTE.—In presenting this paper I beg to acknowledge my indebtedness to the lectures of Prof. Collier Cobb, and to his work and that of Messrs. Chas. Baskerville, R. H. Mitchell and other members of the class engaged in advanced work in Physical geography; but the mode of presentation is my own and I alone am responsible for any short-comings it may have. As my paper was presented for the Kerr Prize in Geol-

ogy it has not even had the critical reading of the head of the department, and lack of funds prevents my presenting as many maps as were contained in the paper.

North Carolina is naturally divided in three sections: (1) The Eastern or Costal plain; (2) The Piedmont Section, and, (3) The Western or Mountain District.

The costal plain runs inland about 100 or 125 miles. "Its western boundry line runs from the western part of Warren through Franklin, Wake, Cumberland, Chatham, Moore, Montgomery, and Anson counties." The whole coastal plain belongs to the Quarternary system, with frequent expanse of the Eocene and Miocene of the Tertiary along the rivers and ravines. As we go inland the country rises about one foot per mile, but from North to South is almost level. Over the whole section the primitive rocks are covered with a deep stratum of earth, principally sand. Along the western border and river courses we find granite, slate, and other rocks sparingly distributed, but no rocks of any kind can be found anywhere else in the region. The section is made up of beds of clay and sand with vast quantities of shell imbeded in them. The upland soil is mostly sandy loam which yields very good crops. There are vast areas of sand that will not yield anything but pines. In fact we know that this whole region has in recent geological time been raised above the sea level.¹

The Piedmont Section begins on the western edge of the coastal plain and runs west to the borders of the Blue Ridge. It is a rolling prairie in the east and gets rougher towards the west, including some small mountain ranges, the Brushy, Pilot, and King's Mountain. The mountain chains of the western part of the Piedmont belt run northeast and southwest; and as the rivers pass them they form rapids and falls that give excellent opportunity for manufacturers.

1. Handbook of North Carolina, 1885, published by Board of Agriculture.

Though you would expect a very rough hilly country on the West you do not find it so. The slope on the eastern side of the Blue Ridge is much steeper than that of the West. West of the Blue Ridge we have a very large valley bounded on the East by the Blue Ridge and on the West by the Great Smoky Mountains. This valley runs northeasi and southwest between the two mountain chains and composes the mountainous districts of North Carolina.

This area has principally crystalline schists and gneisses with patches of conglomerates, sandstones, and shales and limestone. Both the Smokies on the West and the Blue Ridge on the East presents an anticlinal structure; the latter often having its monoclinal member absent. The area was in all probability once covered by an eastern extension of the Paleozoic rocks of East Tennessee, the sandstones of the western district being probably Cambrian (Chilhowee or Potsdam), the patches of limestone probably Silurian, and the grits and shales farther East possibly Carboniferous.¹ I assume that the folding that produced the Appalachian System was, as in Pennsylvania, rapid enough to deform the river systems. It gave rise to four great systems in North Carolina. The first we may call the Deep River syncline. It had its head in Chesterfield County, South Carolina, on the North Carolina line and ran northeast into Virginia. The second had its head in Caldwell County, North Carolina ran east of northeast and joined the first in Virginia. This one may be called the Dan River syncline. The third had its head in Catawba County, North Carolina, and ran south into South Carolina. This may be called the King's Mountain syncline. The fourth, which we may call the Ashe² syncline was rather a canoe-shaped basin with a length of about 150 miles and a width of 20

1. Professor Collier Cobb's Lectures on General Critical Geology, 1893-94; see also Cobb's Map of North Carolina, 1887.

miles in Watauga county and 50 miles in Henderson. Its ends are in Virginia and Georgia, and it took a Northeast and Southwest course. It was probably a lake for a long time until it flowed over, most probably in Henderson county. We find evidences of shores in Transylvania county that were evidently made by a lake. These synclines and the rivers that occupied them may be seen on map (1) It can be seen from the map that the original drainage of western North Carolina was not as it now is. Yet the present rivers are in many cases in the original river beds. The original river of the Asheville syncline headed in the northwest with what is now New river, ran southwest and crossed near Boone into the head waters of Watauga river, ran along the head waters of Watauga, but in the opposite direction taken by the Wautaga now, for a few miles and crossed into the head of what is now Linville river, ran down the stream for about 20 miles and crossed into Brush creek and then into Toe river. At this point Linville river now enters what is known as the gorge. This is a very deep valley that has been cut since the original drainage we are describing. The river that cut through this great plateau has captured the Linville river and led it through, but at the time we are describing this gorge did not exist and the natural outlet was through Brush creek as stated. The river continued down Toe river as far as the fork known as South Toe, and there it crossed the present gap known as the Toe river gap. Down Swannanoa to French Broad and up French Broad and out through Mud creek into South Carolina, thence to sea. The drainage on the southwest began with the Hiwassee river which has since been captured and inverted, and ran east or a little south of east to Valley river, up Valley river, across Red Marble Gap and into Nantehala river, down this to its junction with Tuckaseege river, thence up Tuckaseege and across what is now known as Road Gap, down Richland creek to Pigeon river, up Pigeon to the great bend and

thence across Hominy Gap and down Hominy into the French Broad, up French Broad and out through Mud creek into South Carolina. We have many of our rivers in the original river beds. The Hiwassee has been captured and inverted but it still occupies the old bed. The Nantehala and Tuckaseege still occupy their old beds though there has been considerable change, a part of the latter having been inverted.

We would expect to find in these inverted rivers evidence of it in their sluggish movement but we must remember that most of them have since their inversion been so much lowered that they are the roughest to be found. The Little Tennessee River has cut a gorge through the Great Smoky Mountains over four thousand feet deep and we could hardly expect a river to be slow and sluggish whose lower waters had been lowered so much. Likewise the French Broad from above Hot Springs is very rough owing to the same fact. On the northwest the New river was made by cutting into the syncline and leading a part of the original river out. In map (I) we see that it is about to cut into the syncline and capture a part of the original river. Its headwaters push forward into the syncline until it has captured the headwaters of the original river and inverted a small part of it. This inverted part having a greater fall will move the divide southwest by degrees; and this continues until it reaches the mountain ranges near Boone which on account of its structure marks its final divide. The next stream that cut into our original river was the Watauga. It cut through the Smokies from Tennessee and led off a portion, but did its best work in determining the divide for the other rivers. The strata not all being of the same hardness we can see why these captures went as far as they did and no farther. When New River was inverted it probably would have led out much more of the streams of the northern and middle portions of the basin but for the fact that there was a ledge of rock that outcropped

about the central part of Watauga county and ran entirely across the basin at that point. These rocks had no influence upon the streams until the streams had levelled the country down to them. Then they formed a natural divide and fixed definitely the headwaters of New River. The Watauga was probably captured by a westward flowing stream on the southwest of these and therefore could not capture any of the New River's headwaters. Further on the south of the Watauga and running parallel to it there is another outcrop of rocks which run across the basin and join the Blue Ridge at Grandfather's Mountain, thus fixing definitely the divide between Linville and Watauga rivers. From this divide the river which goes south is Linville, which runs in the channel occupied formerly by the original river. This channel has the highlands of the Blue Ridge on the south and east; and on the west there is a range of mountains which separate Linville and Toe River. Linville River now runs down this valley about twenty miles and then enters what is known as the gorge. The original river formerly passed over and went down Brush Creek, Linville gorge not having been cut at that time, to Toe and down Toe as far as where South Toe enters. The Linville gradually gnawed its way back through a vast plateau and tapped the original river, thus leading off a few miles of it. We will also note that Linville is the only river that captured a stream from this basin and led it out to the east, all the rest have been captured and led off to the west through the Great Smokies.

The next capture was that of the headwaters of the Toe by the Nolichucky. This led all the North Fork of the original river out except the Swannanoa which still retains its old position. As the Nolichucky cuts through the Smoky Mountains it gradually lowers its channel and lowers the whole of the river. As the Nolichucky cuts its way back it furnishes a shorter route to the lowlands and being shorter it has a more rapid current which cuts

its channel faster and the divide migrates eastward until it is finally permanently located at Toe River gap, all the waters of the northwest having been captured by westward flowing streams. The next capture I shall take up belongs to the southwest tributary of the original river. The Hiwassee originally formed the headwaters of the river that drained the southern end of the Asheville syncline and led its waters up to the French Broad and thence out by that river. It is almost if not quite impossible to determine which of these captures took place first and in what order the others followed, but I am inclined to think that the rivers of the northeast were captured pretty much in the order that I have treated them, i. e., the headwaters (New River) were captured first, then a new stream cut in and took another deal off the head and so on down; in the southwest it is most probable that they did take this order. Considering the amount of erosion that the Little Tennessee has done I think that that stream was the first one to cut through and make a capture, thus draining all the basin west of the Balsam Mountains. Later the Hiwassee was captured and inverted and now runs out the southwest end of the basin. We can see by comparing the sketch of the original drainage with the map of to-day that the capture would turn a large volume of water through the Little Tennessee's gorge and thus help to sink it very rapidly. This is most probably what happened. As evidence of capture and inversion in the Little Tennessee River we have several rivers coming into it like the barbs on an arrow; i. e. they show their former tendency to run the other way. The Hiwassee also has several branches coming in in that manner, as the Nattely River and Shoal Creek. In map (I) we can see the river system of the Asheville syncline as it originally was. We see the little Tennessee and the river that captures the Hiwassee just cutting through the Great Smoky Mountains and looking in upon their prey. They are moving their respective divides to the

east and this continues until the divides have moved to their present position, and by this time the Little Tennessee has captured and inverted all the waters west of the Balsam Mountains and the divide has moved to Road Gap where it stops on account of the rocks that outcrop here. The Hiwassee is gradually overcome and captured in a similar manner. This only leaves Pigeon in its original position and running over what we now call Hominy Gap to the French Broad, and on the west we see the river that is to capture it cutting through the Smokies and gradually capturing its headwaters until they are finally all captured and led out through the Smokies. The New Found Mountains form a barrier between this river and Hominy Gap—the bed of the original stream is still the lowest gap in these Mountains.

The creek that flowed from the gap to French Broad is Hominy Creek and since the days of the readjustment it has recaptured two of its old tributaries; i. e. the two small branches that once ran to Pigeon River, now run into Hominy Creek and thence to French Broad*. All these waters that originally found their way to the sea through the upper French Broad valley would have made a large valley and such we find to-day. This stream has been cut into and captured by a stream from the west thus inverting the French Broad from its original course. The French Broad from the mouth of Swannanoa to Brevard, a distance of about forty miles, is a very smooth, sluggish river, so slow in its movements that one can but notice it and compare it to other mountain streams that usually go so rapidly. This is evidence of an inversion which has evidently taken place. From Asheville west, the French Broad is noted for its beauty, which consists in its rough, rugged course over rocks and through gorges, winding its way through the Great Smokies into the Appalachian River. There is very little fall in the French Broad between Brevard and Asheville while between Asheville

* National Geographic Magazine, vol. I, no. 4. By Bailey Willis.

and Paint Rock there is a great fall. At Asheville the altitude of the river is about 2100 feet while at Paint Rock it is 1264, thus giving a fall of 181 feet to the mile. The town of Brevard is lower than Asheville but both towns are above the river. However I believe that there would not be a difference of many feet in the altitude of the stream at the two places. We can see from map of the original drainage the French Broad as it ran southeast, with the river that is about to capture it cutting through the Smokies and having their divide just east of the Tennessee line. As in the other cases the divide has migrated east and the western river has captured and inverted the French Broad and led it out to the west. This finishes up the Asheville basin or syncline. Now let us look at the others. The next one I will take up is the old Dan River syncline which I have described above. It has had two changes. First it has been cut into by the Yadkin which has led about 50 miles of the Dan River headwaters to the sea through its channels and secondly it has had numerous readjustments through its headwaters and those of John's River, a tributary of the Catawba. In the drawing of the original drainage, map (I,) we can see the position of this syncline which originally extended into Virginia and met the Deep River syncline. In the drawing we see that the Yadkin is about to cut into the Dan and as soon as it cuts through it will take the waters to the sea because having a shorter distance to go it must have a greater fall and will hence take the Dan in preference to being captured. The Dan was thus turned from its course and led to the sea by the Yadkin. The present Dan River has a branch, Town Fork, that still follows the old bed. The headwaters of the Yadkin have extended themselves still further north and are now known as the Ararat River. We will now turn our attention to the captures made in the headwaters of the syncline; and this brings me to mention a fifth syncline in North Carolina which I had not noticed until after I had

begun my work on this paper. This syncline we may call the Round Knob syncline since Round Knob is in the syncline and near its head. It began in the west of McDowell and ran a little north of east through Burke and Iredell counties, and it is probable that it continued through Davidson, Randolph and Chatham and joined the Deep River syncline in the latter county although we have no definite evidence that it did. In Map (I) we can see the drainage of this syncline as well as the captures which its waters made on those of the Dan River Syncline. I was at first disposed to think that John's River had captured the branch of Yadkin called Yadkin and that later it had been retaken by the Yadkin, but upon examination I find that those branches near the head of the Yadkin come down from a high plateau and enter the Yadkin at right angles and I am convinced that the branch called Yadkin is merely conforming to the family trait and has never been captured by John's River. If we look at the branches now called John's River and Buffalo Creek we find they have the Yadkin family traits and they show they have been captured by John's River. As the Yadkin cut into and captured the Dan so the Round Knob Syncline has been cut into by the Yadkin and probably by the Catawba and its waters have not gone through the Deep River as they probably did at first. Third Creek is probably nearest the old channel that traversed Round Knob Syncline. The Catawba that cut into the Round Knob Syncline ran a little east of the King's Mountain Syncline originally and it was its tributaries that cut through the eastern side of this syncline and led its waters out. The River that originally occupied the syncline was most probably what we call West Fork of Catawba River. This joined the Catawba where it passes to South Carolina. We see from the original diagram that the tributaries of the Catawba are about to cut through the eastern border of the King's Mountain syncline and lead its waters to the Catawba, and as time

passed we see they kept pushing to the west until they have obtained the position they now occupy. Dutchman's Creek has cut through and branched in the syncline and now drains the whole of it. West Fork of the Catawba which was originally in the syncline has cut through the western border and now drains a large area northwest of the syncline; thus in time the rivers have changed their positions and have so greatly eroded the syncline that we only find traces of it left, such as Anderson and King's Mountain on the west, and on the east not even so much, however we can trace its borders between Dutchman's Creek and Catawba.

The Deep River syncline headed in Chesterfield county South Carolina, and ran northeast to Virginia where it joined the Dan River syncline. We can see its position by turning to the general drainage Map of North Carolina after the Permian uplift, (Map I). Its eastern border still makes the fall line in our rivers, but its western borders were not so well marked, and did not have so definite a boundary. In fact the eastern border was a wide spread of country gradually sloping into it. The eastern border may be seen by drawing a line from Cheraw, South Carolina, northeast passing about ten miles east of Raleigh and striking the Virginia line where Dan river enters North Carolina. Along this line is an outcrop of a number of the older rocks, principally granite. (Hand Book of North Carolina, 1886.) And a little west of this is the old Deep River bed. The river headed in South Carolina with Brown's Creek and ran northeast to the Pee Dee River which formed a part of its bed, up what is now Little river, across to Wolf's Creek, down this to Deep river and down Deep river to Haw river where it turned up what now is New Hope river and across to Stone Creek, down this and up Knopf of Reed's Creek across to Tar river, up this, and to Fox Creek, over to Grassy Creek and down to the Dan river. At this time the coast line was only a few miles east of

this and the rivers such as Roanoke, Tar, Neuse, Cape Fear and others had not cut back to the syncline, however the distance to the sea was small and the fall was comparatively great and they were gradually cutting away. In drawing (Map 1) we can see how they cut this original deep river up and send their streams on westward for other adventures. The Great Pee Dee cut into the syncline near its head and led off Brown's Creek and inverted and led off Little river, then sent one of its streams on northwest and at last under the name of the Yadkin it cuts into the Dan River Syncline and captures a large part of its head-waters as we have described above. Cape Fear cuts into the syncline and leads off the part we now call New Hope and sends its branches on to help drain the territory northwest of the syncline (note the slowness of New Hope River). The Neuse cuts in and leads off a small portion as does the Roanoke, and thus helps the waters to find a shorter route to sea. At last this syncline leaves us this remnant of its former self as evidence of what it has been. The inverted creeks and rivers are yet at a loss to know what to do and so move along slowly, but by and by when they get accustomed to their new environment they will pick up their spirits and move along joyously as they did of old, and later generations will never know what a deal of trouble they have had. Their rate of flow is probably even now being accelerated by the lowering of the eastern border of the central plain.

REDUCTION OF CONCENTRATED SULPHURIC ACID BY COPPER.

BY CHARLES BASKERVILLE.

In a previous communication¹ the writer noted that copper was acted upon by concentrated sulphuric acid

¹This Journal, 17, 90.

(1.84 sp. gr.) not only at the ordinary temperatures of the air, 20°–30°C., but at zero as well. Andrews¹ states that the assertion is incorrect and that it does not occur until the temperature 86°C. has been reached, or a point above the dissociation temperature of the concentrated sulphuric acid, 67°C. according to him. Andrews further says that the author's statements were based "not upon the demonstrations of the formation of sulphurous acid, but solely on the formation of copper sulphate," which, he says, occurs only "in consequence of the presence of the air." It is to be regretted that Dr. Andrews did not note carefully the statements of the author in his previous communication, as no reason whatever exists for any such conclusions, because it was distinctly stated that not only the copper as sulphate, but as sulphide was determined, as well as sulphurous acid, and moreover, that the experiments were carried out when the air had been replaced by a neutral gas, either hydrogen or carbon dioxide.

The author, although confident of the correctness of his former statement, carried out further experiments to correct the error, if committed or to establish, beyond question, the fact that concentrated sulphuric acid of 1.84 sp. gr. is reduced by copper below 86°C., the limit *positively* set by Dr. Andrews.

The fact that these experiments but confirmed the former statement of the author allows the incorporation of the results in this paper.

As far back as 1838 the fact that copper is acted upon by concentrated sulphuric acid at ordinary temperatures, if sufficient time be given, was made known by Barruel². Calvert and Johnson,³ however, failed to obtain any action below 130° C., and considered that none took place.

¹ J. Am. Chem. Soc., 18, 253.

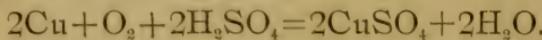
² J. de pharm., 20, 13, 1834.

³ J. Chem. Soc., 19, 438, 1866.

Pickering¹ however stated that "sulphuric acid attacks copper at all temperatures from 19° C., (and probably even still lower) upwards."

First Experiment.—Copper ribbon in strips, 1 x 3-4 cm., was submerged in concentrated sulphuric acid in a clean glass stoppered flask for a month. At the end of that time not only were there white crystals of anhydrous copper sulphate clinging to the sides of the containing vessel, but there was a very appreciable amount of brownish black cuprous sulphide and sulphur dioxide was easily detected by its strong odor when the vessel was opened.

Andrews² states "that in the presence of air sulphuric acid is attacked by copper at ordinary temperatures, but without reduction of the acid. The reaction must take place according to the equation,



Formerly the author³ stated that the presence of the oxygen of the air when it comes into contact with the copper in the acid has great influence on the reaction. Fifty years ago, Maumené⁴ proved that when a current of oxygen gas was passed through the boiling acid, the amount of insoluble residue, *e. g.*, cuprous sulphide, was diminished, that is, less than there would be formed if the experiment were carried out with a current of carbon dioxide. The copper must be directly opposed to the oxygen by only partial submersion or the bubbling of the air against or around the submerged copper; but the air in a confined space, not at all in contact with the copper, but separated by a thick layer of concentrated sulphuric acid, has little or no effect.

Yet grant that the oxygen of the air (volume of air

¹ *J. Chem. Soc., Transl.*, 1878, 113.

² *J. Am. Chem. Soc.*, 18, 252.

³ *Ibid* 17-912.

⁴ *Am. Chem. Phys.* 1846 [3], 18, 311.

about 200 cc.) confined in the flask, had been utilized in the formation of the copper sulphate produced. According to the formula given above; the oxygen would be absorbed and no corresponding amount of any other gas would be eliminated; consequently there should a greater external pressure at the close than at the beginning of the experiment. When the smoothly fitting glass stopper was removed, not only no extra external pressure was noticed, but in fact a pressure from within. This was evidently produced by the sulphur dioxide generated. The sulphur dioxide was swept out by a current of air through a dilute solution of potassium permanganate, which was quickly bleached. The presence of sulphur dioxide was further proven by the addition of barium chloride to the bleached potassium permanganate solution. Nor does the formula given above account for the cuprous sulphide which is always produced.

Second experiment.—Realizing the possibility of some organic matter or dust remaining in the flask, although it had been carefully cleansed, the first experiment was repeated with the greatest precaution to ensure the absence of dust. The flask was scoured with boiling concentrated pure sulphuric acid containing potassium bichromate and carefully cleansed with distilled water. The last traces of water were removed by four subsequent washings with the same kind of concentrated acid used throughout the experiments. The experiment was carried out in the same manner as the first, the same results being obtained.

A blank experiment was carried out at the same time. The flask was rendered dust free in the manner just mentioned and fifty cc. of the same acid allowed to remain in the flask for six months. At the end of that period not a trace of sulphur dioxide could be detected in the blank, therefore the sulphur dioxide produced when the copper was inserted could not be due to the reduction of the sulphuric acid by an extraneous substance, but

solely by the copper. The conclusion is that sulphuric acid is reduced by copper when air is present at the ordinary temperatures, 20°-30° C.

Third experiment.—An ordinary Kjeldahl digesting flask was made dust free by the treatment noted above. 100 cc. sulphuric acid, 1.84 sp. gr., were placed therein and clean dry strips of copper ribbon were completely submerged in the acid. Now air-free carbon dioxide was passed through the flask for three hours. The inlet tube was just dipped into the acid. The flask was then attached to a suction pump, with a sulphuric acid drying flask intervening to prevent a possible return flow of gas or air which might carry moisture or dust into the flask. The flask was exhausted of the carbon dioxide present for three hours at a pressure of 150 mm. It was then sealed with the blast lamp and placed aside in a darkened cupboard. Observations were made every few days to note any reaction taking place. Within two days it could be easily seen that copper sulphate had been formed and the liquid was somewhat clouded by very finely divided suspended cuprous sulphide. Continued observations extending over a period of seven weeks showed only an increase in the amounts of both of these substances. The temperature of the cupboard had at no time risen above 20° C., and was for most of the time much lower. The flask was then opened as any other sealed tube, and instead of an external pressure inward, which had been sufficient to heavily dent the tube in sealing, there was a strong internal pressure outward. The gas evolved was sulphur dioxide, easily detected by its strong odor and bleaching effect upon a dilute solution of potassium permanganate. The sulphuric acid produced by the oxidation of the sulphur dioxide by the permanganate was precipitated by barium chloride. All solutions and apparatus were proven to be free from traces of sulphur dioxide and sulphuric acid by a blank experiment.

Conclusion.—Concentrated sulphuric acid, 1.84 sp. gr.,

is reduced by copper when air is absent and at temperatures far below 86° C., in fact at the ordinary atmospheric temperatures with the formation of copper sulphate and cuprous sulphide and the production of sulphur dioxide.

Finally.—Apparatus similar to that made use of by Andrews¹ with the modification of having three drying flasks containing concentrated sulphuric acid instead of one, and a Meyer absorption tube was substituted for a single small flask. These served merely as extra precautions against dust and insured an intimate mixing of the outgoing gases with permanganate. Within twelve hours the permanganate was bleached. Andrews' experiment lasted only fifteen minutes. The presence of the sulphur dioxide produced was easily detected by the odor when the apparatus was opened, and in the bleached permanganate solution by barium chloride. Copper sulphate and cuprous sulphide were formed.

Concentrated Sulphuric Acid is Acted upon by Copper at Zero.—Quantitative experiments were carried out by the author when the concentrated sulphuric acid in which the copper was submerged was practically at zero.² In stating the results, however, the author gave the temperature as "0°-10° C." The flask containing the acid was buried in an ice-bath and the temperature of the liquid noted by a thermometer inserted through a rubber stopper. The apparatus was air-tight. A stream of hydrogen gas was continued through the apparatus in one experiment for six weeks and in another two months. On two occasions when the ice in the bath had melted in going over Sunday, the temperature rose to 10° C. The temperature could not possibly have remained that high for over twelve hours, which would have had small influence when the experiments lasted through a number of days. The temperature was reported 0°-10° C., how-

¹ J. Am. Chem. Soc., 18, 251,

² Ibid, 17, 908.

ever. Not only copper sulphate, but cuprous sulphide and sulphur dioxide had also formed. Copper, therefore, decomposes concentrated sulphuric acid (sp. gr. 1.84) practically at zero.

From my own experiments and from experiments performed with apparatus similar to that used by Andrews and under the same conditions, except in regard to the important element, time, which consideration is necessary for all chemical reactions, the author must adhere to his former statement.

THE USE OF THE PERIODIC LAW IN TEACHING.

Read before Am. Asso. Adv. Science, Buffalo, August, 1896.

Only a few years after the announcement of the periodic law, when as yet it had attracted little attention, Lothar Meyer pleaded for its introduction by teachers of Inorganic Chemistry so that something of the orderliness observed in organic chemistry might begin to appear in the study of the inorganic elements. A casual examination of the text-books of the period and indeed of those for a number of years afterwards, would show the great need of some such system. Again the great German teacher twenty years later appeared before the Chemical Society at Berlin and threw the weight of the experience of these added years and all his enthusiasm in favor of a thorough use of the periodic system in teaching inorganic chemistry.

Some system must be adopted in teaching this branch of chemistry or the task is hopeless. What will you use if the periodic system is rejected? Some have answered this by using the old families where the elements are arranged by chemical analogies. Even in these families

the influence of the periodic law is deeply felt as any one can see by examining into their condition a dozen years ago and comparing it with the present. Still they are a most unsatisfactory guide to the truths of the science. Some have maintained that the periodic system was little more than those same old groups or families. That shows great ignorance, and a most superficial study of the periodic system. It does include all that was of value in the old groups but much more besides.

The history of the atomic theory is repeated in that of the periodic system. It is now meeting something of the opposition and even denunciation which the atomic theory met with in the third and fourth decades after its announcement. The unexplained exceptions to it are being magnified and many are inclined to think them insuperable and to look with doubt upon the entire system, while some are ready to throw it overboard as rubbish past its usefulness.

I do not think that in these classes of opponents will be found any who have made patient and thorough study of this system. To me, the more I study it the more its interest and value grows and the more fascinating the search after the great truths which unquestionably lie within it and of which it yields glimpses even in its incomplete state. For the system is incomplete. It cannot well be otherwise until our knowledges of the science is broader and deeper. It will grow with and direct the growth.

But in its incomplete state it is amply sufficient to act as a most helpful guide to the study of inorganic chemistry. It introduces order and clearness where such were previously, in large measure, lacking. It saves much useless repetition and so brings about conciseness and brevity, a saving that appeals to both teacher and pupil. There are few earnest students who will not become enthused with the wonderful symmetry of the science and hence of all nature when this Natural System is unfold-

ed to them. I have had a student come to me with the confession that he had been able to see nothing of the attractive beauty of the science in his study of it until this system brought law and order into what had only been confusion to him before.

The brief time allotted to me gives opportunity only for an earnest plea in behalf of the introduction of the system and does not admit of an extended exposition of the application. An excellent guide along this line will be found in the lecture of Lothar Meyer before the German Chemical Society which I have already referred to but let me say that the only truly successful way of teaching this system is for the teacher to make a faithful study of it and its capabilities for himself. It is not the old system of families and it is not to be treated merely as affording a convenient classification. All that was true in those groups it retains but it further develops and in a measure explains them.

A few of the lines of usefulness of the system may be pointed out. First arbitrary distinctions, such as between metals and non-metals, which have given chemists so much trouble to define and maintain, can be done away with. The Berzelian division into electro-positive and negative elements is revived and fixed and enables one to account for the gradations between these elements.

The system gives a simple, easily remembered and applied arrangement of valence in the place of the confusion and difficulties of the old methods.

The full introduction of the periodic system means a consecutive study of the elements as allied bodies. This in a measure resembles the study of the hydrocarbons in organic chemistry. It is very valuable as giving a connected view of these bodies. The symmetry of chemistry is better shown and the student feels that he has a grasp of the whole, an intelligent comprehension of the properties chemical behavior and inter-relations of the elements which he can scarcely arrive at by the old way.

When it comes to studying the compounds they are studied connectedly. Thus the hydrides of all the elements, are examined, giving their relation to hydrogen; then the oxides and the influence of the negative and positive nature of the elements upon their relation to oxygen and hydrogen. Under the head of each acid (for the acid largely determines the general characteristics of the salt) the various salts are discussed. This gives a better understanding of the characteristics, saves repetition and tends to fix in the memory the compounds or classes. And so too the constant taking up of the elements in their groups and series fixes them in the mind.

I cannot give the system in detail. Study the periodic system and Meyer's lecture carefully and then laying aside prejudices and traditions go boldly to work. What I have stated about the advantages of the system may seem overdrawn. The statements are based upon an experience of three years and no one has the right to gainsay them until he has faithfully tried the system.

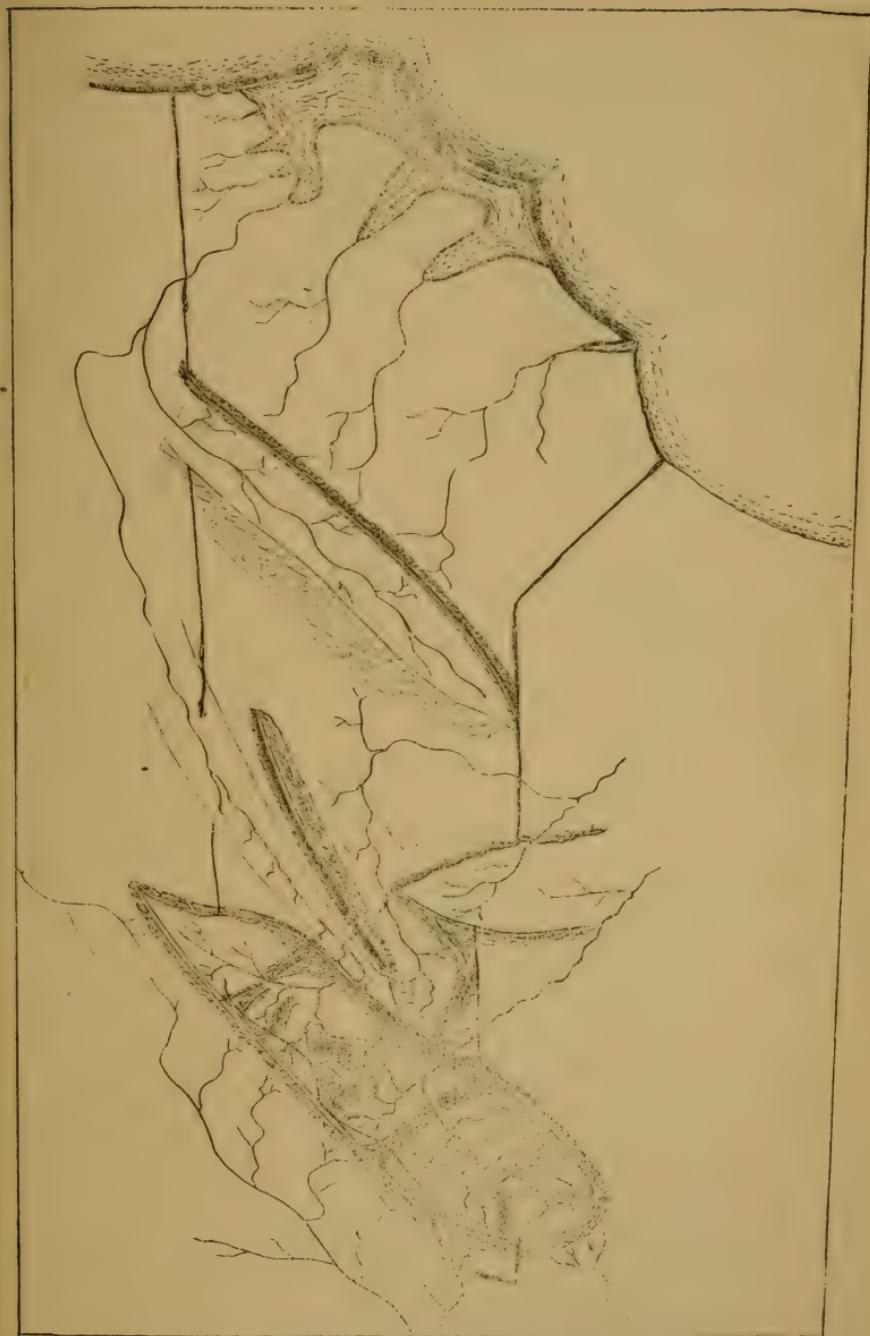


Fig. 1. Original Drainage.

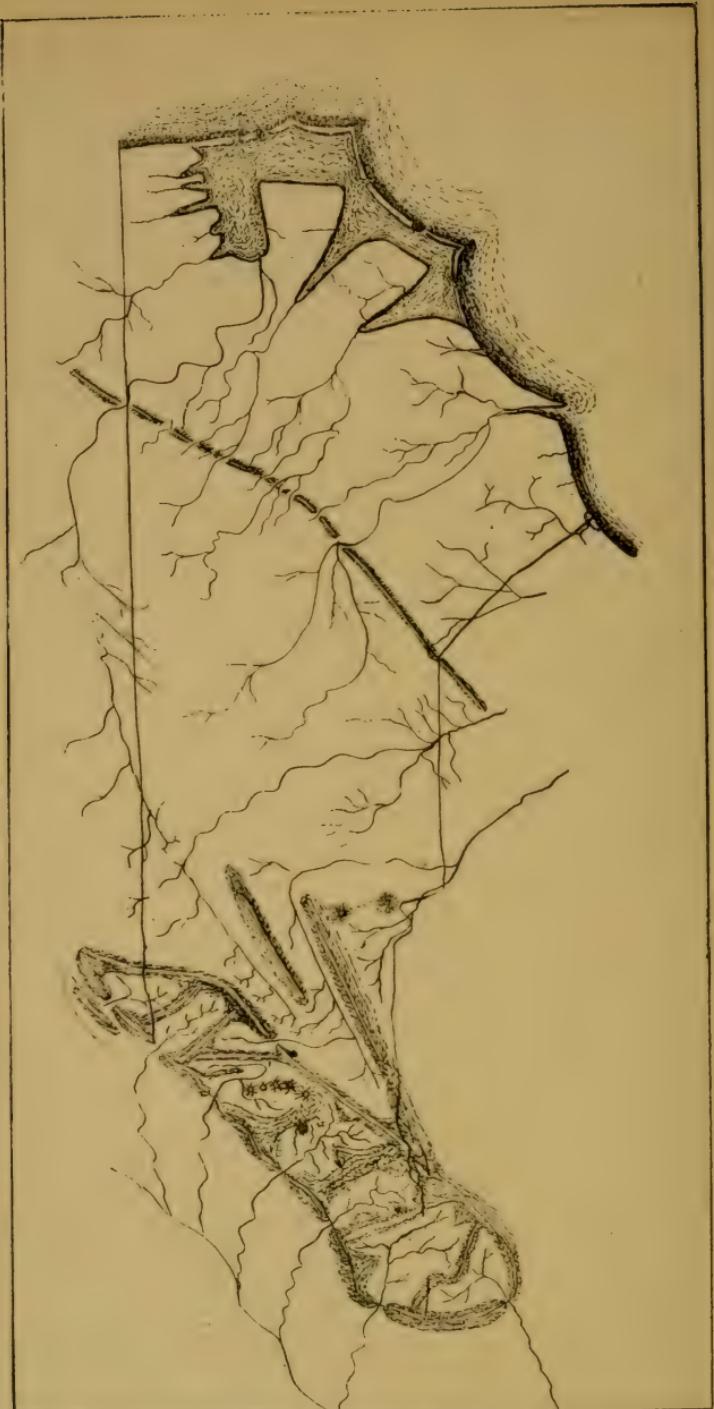


Fig. 2. Present Drainage.

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THE PRESENT POSITION OF THE PERIODIC
SYSTEM.

The atomic theory, (first announced by Dalton in 1803) has for nearly a century formed the basis of Chemistry as a science. It is still the only plausible explanation of the vast array of facts gathered by chemists of all ages and forms the web and woof of all modern chemical theories. It has been the object of prolonged discussion and attack, but having withstood the storms of nearly a hundred years, its acceptance now is full and it has become so ingrained into the chemist's conception of his science that he looks upon it almost as one of his facts, a foundation stone of his building and seldom stops to realize that after all it is only an assumption, an hypothesis, a theory. To shake it would sadly disturb the fabric of his science.

A little more than twenty-five years ago with the announcement of the Periodic Law by Mendeléeff this atomic theory reached its highest development and gave its clearest promise of finally leading up to the solution of the true nature of matter. Like the original theory, this development of it received but tardy recognition but the sense of its importance has grown until it stands to-day the central fact of chemistry. Through it new zest has been given to research in fields from which it was thought the harvest had been gathered. It has given a new object to the chemist's work. It systematizes and arranges all the facts which he gathers. It gives a compactness and symmetry to his science unknown before. It brings a step nearer the realization of that dream of the

ages—the Unity of Matter. It may be said, with truth, that the Periodic System is the science of Chemistry itself. As such it must of necessity be incomplete. Through it we have been forced to realize how incomplete our science really is. In one sense, then, to study the present condition of the Periodic System would be to study that of chemistry. We will examine the question, however, from another and more restricted point of view.

We may, in discussing the present position of the Periodic System, draw a distinction between certain points which are well established and others which are still under discussion or beyond our grasp at present.

First it is clear that the natural arrangement of the elements is in the ascending order of their atomic weights. This arrangement proved a failure when attempted by Gladstone because of imperfect atomic weights. In the hands of de Chancourtois, Newlands, Meyer and Mendeléeff it was developed and the singular relations between the elements, called periodic, were made apparent. This brings us to the second point, that when the elements are arranged in the order of their atomic weights they fall naturally into certain analogous groups and periods with a recurrence, or repetition, of properties at certain intervals. This leads up to the third point which we may acknowledge as fixed, namely that the properties of the elements are determined by and dependent upon the atomic weights. This was first stated by de Chancourtois, was proved independently and from a different standpoint by Hinrichs and was forced upon the attention of the world by the genius of Mendeléeff.

The points which still remain to be settled are very numerous. In the first place the number of the elements is unknown. Clarke, in the recent revision of his classic recalculations of the atomic weights, gives a list of 74. This leaves out of account all whose atomic weights are still very imperfectly determined or whose existence is still in doubt. Mendeléeff's table allows for the existence of

106 elements if a sub-period between hydrogen and lithium be granted. Meyer's table contains 79 spaces, or counting a similar hydrogen period 86 in all. If helium and its mysterious companion really have the two atomic weights assigned them, the assumption of this hydrogen group will become necessary. If Mendeléeff is right, then not more than three-fourths of the elements are at present known to us. The vacant space allowed by Meyer for new discoveries is much more reasonable and probably not much in excess of the demand of the near future.

Of the 74 recorded by Clarke less than one-half have the atomic weight determined with accuracy to the first decimal place. As Clarke says: "In most cases even the first decimal is uncertain, and in some instances whole units may be in doubt".

As the entire arrangement is dependent upon the atomic weights it is manifest that the doubt attaching to those in use seriously retards the development of the system. Some points of great interest must be left entirely in abeyance until data for accurate reasoning are at hand. The atomic weights of the first third of the elements are among the best known and this justifies the arrangement of those imperfectly determined. We would otherwise scarcely be justified in laying much stress upon the periodic arrangement.

The imperfectly known atomic weights makes it impossible to assign positions in the system to some of the rare earth elements and certain of those more recently discovered. If some of the atomic weights assigned those elements at present are even approximately correct then it seems to be impossible to give them their proper places in any of the more prominent tabular arrangements of the system.

This matter of the tabular arrangement of the elements is one which is very far from settled at present. Mendeléeff offers two arrangements, one in vertical, the other

in horizontal series. They differ widely in many important points. Some teachers make use of one, some of the other. The Germans and many teachers in England and America use Meyer's horizontal table. Many other tables have been proposed but they differ widely from those of the two great discoverers of the Periodic System and are generally intended to present and advocate some scheme as to the Genesis of the Elements or some other wild and questionable fancy.

I may be pardoned a brief reference to the table worked out by myself and suggested as an aid to teachers. It does not depart very far from the Mendeléeff horizontal table, but my own experience has proved it to be more easily taught and more quickly learned and hence very valuable for the teacher. It certainly brings out some facts which no other table presents, and when our knowledge is fuller it may aid in solving some of the puzzles now connected with the system.

It must be said that none of the systems are satisfactory, all are imperfect and incomplete and must remain so until our knowledge of the science is itself complete. Recent growth in the science has shown the insufficiency of the older arrangements. The discovery of argon and helium (and shall we add asterium?), the repeated determination of the atomic weights of iodine and tellurium and of the nearly twin elements cobalt and nickel showing them to be out of place in Mendeléeff and Meyer tables, have proved surprising reverses to the system after the brilliant successes of its earlier history. In the first table the existence of new elements had been predicted with an exact statement of their properties. These predictions had been marvellously fulfilled in the discovery of scandium, gallium and germanium. It was to be expected that future discoveries would only strengthen that which was already so strangely confirmed. But these new elements, argon and helium, were not predicted and refuse to be fitted into the system, as at present constructed, and are

altogether obstinate and refractory. In the minds of some the whole system seems overthrown. Let us have patience a little while until the light is clearer and both systems and these elements are better known and understood. As Winkler recently said before the German Chemical Society (Ber. d. Deutsch Chem. Ges. 30. 19) "Es erscheint nicht ausgeschlossen, dass die Entdeckung der beiden neuen Elemente Argon und Helium Anlass zum weiteren Ausbau, wenn nicht zur Umgestaltung, des periodischen Systems geben wird, wobei vielleicht auch gewisse, jetzt noch vorhandene Unsicherheiten und Widersprüche ihre Lösung finden werden."

It must not be forgotten that these tabulations began their existence with a serious blot upon them, an unsolved puzzle. From the very beginning no logically satisfactory position could be nor has yet been assigned to hydrogen. There have been sundry attempts at doing this, it is true, but they are not satisfactory and so the standard element, in some respects the most remarkable and important of them all, is without an abiding place in the home of its brethren. It would seem to be the play of Hamlet with Hamlet left out.

That these tabulations of Mendeléeff and Meyer are regarded as imperfect and unsatisfactory is shown by the large number of tables suggested within the last decade. Reynolds, Reed, Flavitzky, Livermore, Tchitchérine, Wendt, Wilde, Preyer, Deeley, Traube, Thomsen, de Boisbaudran are some of the names connected with these tables. They serve to show that many minds are attacking the problem and give much hope for the future. If the clear, pellucid truth can be filtered away from the wild and fanciful and false the progress will be more rapid.

Our little systems have their day,
They have their day, and cease to be.

So far, no really good method of graphically illustrating the Periodic Law has been suggested. The spiral

used by de Chancourtois in his really remarkable work has been the favorite method of illustrating it. It has been followed by Lothar Meyer, Mendeléeff, Gibbes, Baumhauer, von Huth, Carnelley and others. Probably a better method for class and teaching purposes is the pendulum-like diagram of Spring, used also by Reynolds and Crookes. Mendeléeff's objection to the curves of Lothar Meyer seems to me valid though many prefer to use these or similarly constructed curves. They are, at any rate, scarcely suited to the needs of the student who is indifferently equipped with mathematical ideas. Two objections can be raised to any and all of these diagrammatic illustrations. In the first place they fail to bring out some of the important conceptions of the system, even obscuring some of the points; and in the second place, they generally include fancies and speculations not essential to this system and not justified by our present knowledge of it. They go too far and like much teaching of science by analogy, are liable to be presented by those using them without due care and precaution. This is especially the case wherever they are looked upon as illustrating the genesis of the elements, about which we still know nothing and should say nothing.

Hartley puts the matter in this way. "The Periodic Law can then be thus stated: The properties of the atoms are a periodic function of their masses. In any graphic representation of the periodic law the fact that it is upon the mass of the atoms that their properties depend should appear prominently. The diagram of Dr. Johnstone Stoney used to illustrate the "Logarithmic Law of Chemistry" has, on this account, alone a pre-eminent importance." This diagram of Dr. Stoney's could scarcely be used by the average teacher because of its complicated nature and the knowledge of mathematical operations required. Surely the greatest requirement is clearness and simplicity. It should appeal readily to the

eye and carry in itself in great measure its own explanation. It should present the details of the law and not some portion of them merely. It should not lead to confusion of thought, nor to erroneous conclusions, nor to unconfirmed dreams and fancies. It is manifest that in the present imperfect state of the system no such diagram is possible. Of all which have been offered I do not know of a single one which is truly helpful, which has not upon it some serious blemish, and so I would give voice to a warning against their use. Some one of the tabulations must serve our purposes for the present as a means of graphic representation.

While it is true that the Periodic System has not told us how these simple bodies which we call elements were generated nor from what they came, while it leaves for the present the so-called Genesis of the Elements a blank and may never contribute anything to raise the vail, it is still true that the System has done much to strengthen the belief in the Unity of Matter and to prove beyond all doubt that these elements are not independent, disconnected units but strangely related and interwoven parts of one symmetric whole. However powerless we may be to decompose these simple bodies and split them up into components, it is becoming every day clearer that they are not truly simple but compound. Of what composed or how, we know not, but through them all there runs the traces of some community of nature. Chemists, in their conservatism, are slow to acknowledge a change in belief, so radical as this, without strong bases of proof, either directly or indirectly experimental. It smacks strongly of the baseless fancies of the early alchemists and the Science cannot afford any more Will-o-the-Wisp chases. But when such great names as those of Wislicenus, Thomsen and our own Remsen lend their weight and influence to the new movement we can follow, using the same caution as our leaders. To quote Remsen "It has been shown by a Russian chemist, Mendeléeff and at the same time by a

German, Lothar Meyer, that the elements are related in a very remarkable way, so closely that it is possible to arrange them all in one table, in which they form parts of a system general. The law governing the variations in properties of the elements is known as the Periodic Law. The limits of this article will not permit any detailed explanation of this remarkable law. The main point that I wish to emphasize is, that the so-called elements are shown to be related to one another and it seems impossible in the light of these facts, to believe that they are distinct forms of matter. It seems much more probable that they are in turn composed of subtle elements and it has been pointed out that all the substances which we now call elements, of which there are about seventy, can be conceived to be made of two fundamental elements combined in different proportions. There does not, however, appear to be any immediate prospect of discovering these fundamental substances."

The Periodic System is giving us a clearer perception of many things and gives promise of a deeper insight into the nature of matter. Yet there are unsolved mysteries connected with these numbers which the chemical world has been puzzling over for nearly half-a-century. What is the meaning of the group-differences and the strange recurrence of certain difference numbers and factors which were noticed by Dumas and Cooke and have fascinated and bewildered a host of others since? Why should the numbers eight and eighteen be so frequently repeated in these differences? Thus we find sixteen as the interval between the atomic weights in the alkali, alkaline-earth, oxygen and other groups (using the old designations). Why should seven be the number of elements in a period? Is there a great law of octaves running through nature, in music, color, and the elemental simple bodies? There is little of practical value to be gotten from such speculations but judging from the large numbers of numerical regularities reported it has proved a seductive field. Lit-

tle is to be gleaned from such work. Strange and puzzling figures occasionally appear but the fanciful erratic nature of most of it can be seen from the connection reduced by some between these numerical regularities and the planetary distances or other matters, equally as far away. Some have sought out mathematical formulas by which the atomic weights might be calculated but without very gratifying success. One of the most persistent dreams of the century, Prout's Hypothesis, seems to have received its quietus for a time at least. Such error is hydra-headed and one can never be sure that all the heads are off.

A grand service has been done Chemistry by the discovery and announcement of this system. Chemists have the short-comings of their science brought clearly to their notice and research which was before somewhat desultory and aimless, a little picking here and there, is concentrated and direct so that the work may tell. And this is well as we enter upon a new century—one whose close is to see us a good hundred years further on than we are now. The gaps must be filled, error eliminated, knowledge perfected, so that we need grope no longer but may walk in the light of truth. The man who takes some little portion of the field and examines the inconsistent statements, and stumbles over the absolute errors, and loses his way along paths upon which research has shed no light at all, must bow his head in shame at the small result of our toil during all these centuries of groping.

Let us then be up and doing. Strive to make some one thing clearer, to brush away some error, or to place one stepping stone securely for the feet that are to follow.*

*Address before N. C. Section Amer. Chem. Soc., F. P. Venable, Raleigh Feb. 22, 1897.

NOTES ON THE EXACT COMPUTATION OF THE QUEEN POST TRUSS.

The Queen Post Truss is extensively used in the construction of ordinary highway bridges, as on account of its simple details it is easily constructed by the average carpenter. As usually built by him, there are no counter braces in the middle panel, so that for an eccentric load, the stiffness of the chord has to be depended upon to transfer part of the load to either abutment. Plate 1 represents a bridge composed of two Queen Post trusses placed parallel to the line of road and sixteen feet apart in the clear. The ends of these trusses rest upon wooden timbers (wall plates) at either abutment and the long vertical rods hold up the suspended beams which extend under the bridge from truss to truss. The joists which hold up the planking of the roadway are placed parallel to the trusses and rest at their ends upon the suspended beams and the wall plates. Any load which comes upon the planking is transferred by these joists, acting as beams, to the suspended beams and wall plates. The load thus transferred to a suspended beam is carried to its ends and thence by the vertical rods to the upper joints of the truss, whence it travels down the rafters or main braces to the abutments. For a uniform load over the bridge both suspended beams carry the same loading and the computation of the stresses in the truss members is made in the usual manner. If, however, a heavy concentrated load, as that due to a road roller or a crowd of people, is supposed to act on only one suspended beam, the investigation is of a different character. The part of this concentrated load which is held up by the vertical rods, meeting at an upper joint of a single truss, will be

called W . At the upper joint, this vertical load W is decomposed by the parallelogram of forces method into components acting down the main brace and along the upper chord respectively. The resulting push along the upper chord is decomposed at the next joint into components acting along the other main brace and vertical. The triangle of forces at this second joint is necessarily the same as that at the first joint, as the horizontal component is the same and the rafters are equally inclined to the vertical. Therefore the stresses in the vertical and rafter at the second joint are precisely the same in character and amount as at the first joint. Hence there will be a tension W , in the vertical rods at the second joint and this tension, pressing the suspended beam upwards against the lower chord, tends to bend it upward. The lower chord is thus in the condition of a beam of length equal to the span and subjected to a single upward force W , acting at one third of its length from one end for equal panel lengths. The force W , causes the lower chord to press upwards against the feet of the rafters, with a force $\frac{2}{3}W$ at the nearest rafter and $\frac{1}{3}W$ at the furthest. As we found the vertical component of the stress in both rafters $= W$, acting downwards, the resultant pressures on the abutments are, $W - \frac{2}{3}W = \frac{1}{3}W$ and $W - \frac{1}{3}W = \frac{2}{3}W$ as should be, by the law of the lever, for the original load W acting at the first joint, the larger reaction occurring at the abutment nearest the load.

The lower chord must be made of sufficient dimensions to act as a beam to safely sustain a vertical force W acting upwards and placed a panel length from one end. The moment is greatest at the force and equals $\frac{2}{3}W$ (its reaction at foot nearest rafter) multiplied by one-third the span or length of lower chord from foot of one rafter to that of the other. In addition, the section of the lower chord must be made large enough to provide for the horizontal component H of the stress in a rafter at its foot. This thrust generally acts at h inches above the center of

the chord, depending on the depth of the notch where the rafter joins the chord, and thus not only causes a uniform stress, in the chord but one due to the moment Hh . The maximum fibre stress in the lower chord at a panel point is that due to the above forces combined with that due to the weight of the chord, for all of these influences cause tension in the top fibre of the chord at a panel point.

With a full live load W at each end of both suspended beams, the stresses in the verticals are W as before. So that the stresses in rods, rafters and upper chord are precisely the same as for the eccentric load first considered. In this case, the stress in the vertical rods = W , is exactly balanced by the load W held at foot of rod, so there is force tending to bend the chord. The dead load stresses are of course to be found and added to those caused by the live load,

The above theory is upon the supposition that the "suspended beams" are not fastened to the lower chords. If they are fastened, a load at one suspended beam only, is partly carried by the chord "acting as a beam" and partly by the vertical ties. Reasoning as before, the stresses in the verticals at the other joint are the same as those of the first, giving an upward pull on the chord where the suspension beams meet it. The lower chord in this case, is bent downward at the load and upwards at the other panel points, thus giving a reverse curvature to the chord, so that it can resist bending much more effectively than in the former case, where it was compelled to act as a beam with a span equal to the span of the bridge and was acted on by a full panel load. The exact solution for this case cannot be effected by statics alone. Another principle has to be made use of and I have availed myself of the principle of least work, for which see an article by the writer in the Transactions of the American Society of Civil Engineers for April, 1891.

In this article, the writer deduced the principle of least work, with effect of temperature changes included, by

the method of virtual velocities, to which it readily lends itself. Castiglione in his "Systèmes Elastiques," a work that deserves to become classic, had already deduced the principle in an entirely different manner and given numerous applications to structures in metal and stone.

The writer has followed essentially his manner of applying the principle, to the truss next to be examined, though by regarding the chord, when acting as a beam, to be "free" under the action of certain forces. there is a gain in simplicity.

I have computed in full, the truss shown in plate 2, an inverted Queen Truss. As it corresponds exactly in theory to the truss shown in figure 1, if we suppose the suspended beams there to rest on or be fastened to, the lower chord, the solution of the one truss will indicate that of the other.

Reference will be made to the following principles in the theory of elastic work:

In a straight bar of length a and cross section ψ , subjected to a gradually applied stress which reaches its maximum s , the elastic work of deformation, c being the coefficient of elasticity of the bar is,

$$\frac{1}{2} \frac{a}{ew} s^2 \dots \dots \dots \quad (1)$$

In a beam subjected to vertical external forces, if we call the length of a segment of the beam $2l$ and the moments of the external forces, at the right end of the segment M_0 , at the middle M_1 , and at the left end M_2 , the elastic work of deformation, of the segment considered is

$$\frac{1}{2EI} \frac{l}{3} (M_0^2 \times 4M_1^2 + M_2^2) \dots \dots \dots \quad (2)$$

E being the modulus of elasticity of the beam.

The principle of least work requires that the sum of the work due to all members of the structure shall be a minimum, when one unknown stress is required.

In the elevation of one truss of the structures shown by fig. 2, the centre line of chord is 45 ft. long and is divided into three equal panels. From centre line of chord to bottom of posts is 4 feet, thus giving the length of inclined rods AC (from washer to foot of post) 15.52 feet and the length of horizontal rods CC 15 feet.

We shall suppose that the two suspended beams on either side of the left post, transfer to the chord through the hangers, a load of 14 thousand pounds and the suspended beams at the right post similarly transfer a load of 4.5 thousand pounds. [All loads, reactions and stresses will be expressed in thousand pounds.]

Call ρ the part of the load 14 that is supported by the chord acting as a beam and therefore $14 - \rho$ will be the part held up by the left post. The downward thrust of the post on the ties gives a stress in the left inclined tie $= 15.52(14 - \rho) \div 4$ and in the horizontal tie, $15(14 - \rho) \div 4$. This last tension, when resolved at foot of right post into components, gives a tension in inclined tie there and compression in post, the same as found at the left apex C, the triangles of forces being equal at the two apices as the stress in the horizontal tie is the same in both.

The right post thus pushes upwards with a force $14 - \rho$, which is assumed, as we shall find it to be, greater than the load 4.5 applied to chord at right post. The difference $(14 - \rho) - 4.5 = 9.5 - \rho$ represents then, the upward thrust against the chord there which must be sustained by the chord acting as a beam.

The chord acting as a beam, therefore sustains a downward force over left post of ρ and an upward force at right post of $(9.5 - \rho)$. By the law of the lever, these forces cause a downward pressure at the left abutment of $(\rho - 3.166)$ and an upward effort at right abutment equal to $(6.333 - \rho)$.

As the vertical components in both inclined rods are each $(14 - \rho)$ we have, as the total pressure of truss on left abutment, $(\rho - 3.166) + (14 - \rho) = 10.833$ and at right

abutment $(14 - p) - (6.333 - p) = 7.666$, just as we should find for the two original loads by the law of the lever.

These results are true for any value of p (< 14) that may be assumed. They do not determine p . We shall soon see how to determine it after expressing the work of deformation of the entire truss in terms of p .

As the elastic work in the vertical posts is very small it will be neglected. The work in the ties is given by formula (1).

For the two inclined ties, the stress, $s = 15.5 \times (14 - p) \div 4$, $a = 15.5$ and $w = .04$ square foot nearly. Substituting these values in (1) and multiplying by 2 we get the elastic work by inclined ties at either end.

Similarly the stress in the horizontal tie CC, $s=15$ $(14-p)/4$, also $a=15$ and $w=.04$. These values substituted in (1) gives the work of horizontal rod CC.

As the modulus e is for iron and E for wood, take $e=16 E$, then the work of the iron ties in one truss will add up to,

on neglecting terms that do contain ϕ , as will be done in what follows, as such constant terms disappear when differentiated as to ϕ .

To ascertain the work on the chord acting as a beam, we use formula (2). We have the downwaad force ϕ acting at left post, the upward force $(9.5 - \phi)$ at right post, the upward *reaction* at left abutment $= (\phi - 3.166)$ and the downward *reaction* at right abutment $= (6.333 - \phi)$. The beam can thus be considered as free and subjected to these forces only.

Let us apply formula (2) first to right segment of chord from E to B, 15 feet in length,

$$\therefore 2l=15,$$

$$M_0 = 0,$$

$$M_1 = (6,333 - p)7.5,$$

$M_2 = (6,333 - p)15$;
giving the work of deformation for this section,

$$\frac{1}{2EI} (1125p^2 - 14250p) \dots \dots \dots \quad (4).$$

neglecting the constant term as before. For the middle segment, $2l=15$,

$$\begin{aligned} M_0 &= (6.3333 - p)15 \\ M_1 &= (p - 3.166)225 - 7.5p \\ M_2 &= (p - 3.166)15 \end{aligned}$$

The work by (2) for this segment is therefore,

$$\frac{1}{2EI} (3375p^2 - 32062p) \dots \dots \dots \quad (5).$$

Lastly for the left segment A B, $2l=15$,

$$\begin{aligned} M_0 &= (p - 3.166)15 \\ M_1 &= (p - 3.166)7.5 \\ M_2 &= 0 \end{aligned}$$

∴ by (2) work equals

$$\frac{1}{2EI} (1125p^2 - 7125p) \dots \dots \dots \quad (6)$$

Adding together (4), (5) and (6) and for a beam 6×16 inches, putting,

$$I = \frac{1}{12} \cdot \frac{1}{12} \cdot \left(\frac{4}{3}\right)^3 = \frac{8}{18},$$

We get as the total work of the chord acting as a beam,

$$\frac{1}{2E} \left\{ 56953p^2 - 541050p \right\} \dots \dots \dots \quad (7).$$

The uniform compression in the chord, $s = 15 (14 - p) \div 4$, causes elastic work given by (1), on substituting, $a=45$ and $w=\frac{2}{3}$ square foot; the amount being,

$$\frac{1}{2E} \left\{ [950p^2 - 26600p] \right\} \dots \dots \dots \quad (8).$$

On adding the expressions (3), (7) and (8), we find for the total elastic work of one truss, neglecting constants,

$$\frac{1}{2E} \left\{ [58960p^2 - 597250p] \right\} \dots \dots \dots \quad (9).$$

By the principle of least work, the derivative of this with respect to ϕ must be placed equal to zero in order to find ϕ .

$$\therefore 117920\phi - 597250 = 0 \\ \therefore \phi = 5.07.$$

So that the chord, acting as a beam, sustains a downward force at the left post of about 5 thousand pounds and an upward force at the right post of 9.5— $\frac{1}{2}$ or about 4.5 thousand pounds, causing the chord to bend down at the left post and upward at the right post. This reversed curve assumed by the chord causes it to be more efficient as a beam than in the preceding bridge examined.

The value of the reactions of the chord, acting as a beam, at the ends, we have seen to be,

$$p-3.17=1.90 \text{ and} \\ 6.33-p=1.26;$$

thus giving the greatest moment at the left post equal to
 $1900 \times 15 = 28500$ foot lbs.

If we allow, by the usual formula, 1200 pounds per square inch fibre stress the chord, for a depth of 16 inches, should be 6.6 inches wide in place of the 6 inches assumed. Certain changes of temperature will increase this width still further as we shall see.

INFLUENCE OF CHANGE OF TEMPERATURE.

The linear expansion of iron, per unit of length, for each degree centigrade (1°C), is $1 \div 82500$.

Suppose the bridge put together at 10°C (50°F) and that

the temperature afterwards rises $t=25^{\circ}\text{C}$ (45°F). If the expanded horizontal bar CC is supposed in position, the end bars AC and EC will each be too long by

$$\frac{1}{2} \frac{15t}{82500} \cdot \cos i + \frac{15.52t}{82500} \cdot .000276t$$

where i = angle that end bar makes with chord.

The tension in end rod or tie is

$$15.5 (14 - \rho) \div 4$$

Twice the product of these two expressions, or,

$$(\text{constant} - .00214t)$$

gives the work due to heat in the truss, neglecting any expansion of the wood.

By the article of the writer referred to above (Section 6), we must add this term to the elastic work (9) of the entire truss and put the derivative with respect to ρ equal to zero. Doing this we obtain,

$$58960\rho - 298625 - .00214/E = 0.$$

If we assume E for yellow pine, 1,600,000 pounds per sq. inch, or, as we must substitute it here, where all dimensions are in feet and loads in thousand pounds,

$$E = 230400 \text{ thousand pounds per sq. foot,}$$

we derive,

$$58960\rho - 298625 - 493t = 0 \dots \dots \dots (10),$$

$$\text{whence for } t = +25(\text{C}), \rho = 5.27$$

$$\text{and for } t = -25(\text{C}), \rho = 4.85.$$

The rise of temperature of 25°C (45°F) above the supposed normal of 10°C (50°F) gives the greatest reaction, 2103 pounds, at left abutment, and hence the greatest moment = 2103×15 foot pounds at left post. This moment calls for a beam 7.4 inches wide by 16 deep. It was made 8 inches wide to allow somewhat for the uniform compression, which, however, is less than 300 pounds per square inch on account of the large section of the chord. At the left post, the weight of the chord

tends to cause tension in the upper fibre. Its influence being beneficial, was not further regarded.

The method has now been given in full for ascertaining the stresses in the various members for a non-uniform loading.

In this particular case, the dead load per panel per truss, was assumed at 4500 lbs., which is found to be nearly exact on making out weights, etc.

The live load was assumed to be that due to a crowd of people weighing nearly 80 lbs. per sq. foot, for a clear width between trusses of 16 feet; the portion held at one apex of one truss being 9500 pounds. As such a partial load can only be obtained by supposing the live load to extend from an abutment two panels and then neglecting the part held up at the farthest apex, it is in excess of any eccentric load that can be placed only at one apex and thus is on the side of safety.

The influence of temperature changes is seen to be very marked for this combination bridge and would be still more pronounced for more northern latitudes, where greater ranges of temperature are experienced than in the Southern states. By giving any desired value to t in equation (10) above, the resulting value of ϕ is readily found and the chord examined as before for proper width.

It would materially tend to obviate the bad effects of temperature if the truss was assembled in the heat of summer without any camber in the chord. As it became colder, the chord would receive a slight camber upwards, which would increase with the fall of temperature, and thus tend to diminish the large bending stress in the chord at the most heavily loaded apex. For this case, we should put, say, $t = -50$ in eq. (10) and thus find $\phi = 4.65$ and finally the resulting maximum moment in the chord acting as a beam which turns out to be at the right post where no live load is supposed to rest. It is 1683×15 ft. lbs., and thus less than for the temperature at which the

bridge is assembled; so that no increase of stress is experienced, but the reverse and the width of chord can be safely taken at 6.6 inches, or say 7 inches, for a depth of 16 inches, as first found.

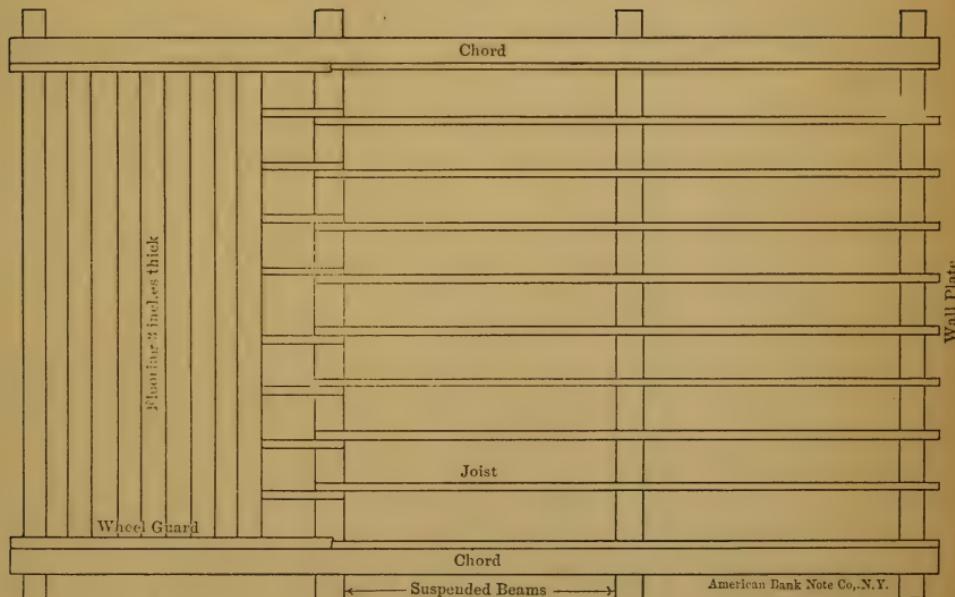
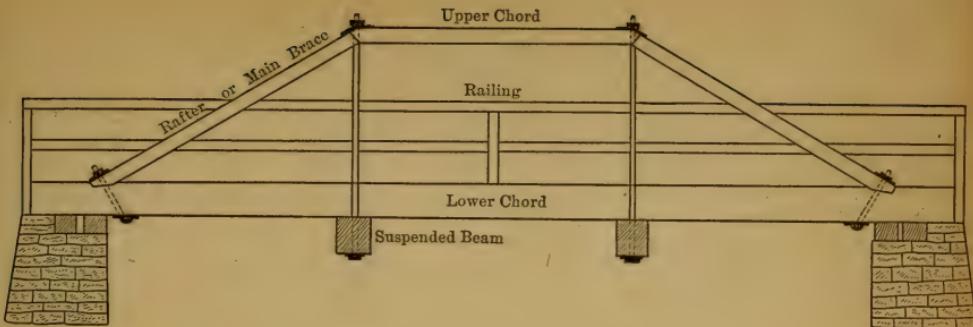
The maximum stresses in the ties and posts are of course under a full loading of 14,000 pounds at each post. The chord now bends downwards throughout so that it cannot sustain near as much of the load (acting as a beam) as before. The strict investigation can be made as above; but it may prove near enough in determining the section of the ties (the posts evidently having an excess of strength) to suppose each post to carry the full panel load in place of the strict value ($14 - p$), to the ties and proportion them for the corresponding stress in an end tie, as their section is uniform throughout. The section given was determined in this way for an assumed unit stress of 10,000 pounds per square inch.

SOME LATE VIEWS OF THE SO-CALLED
TACONIC AND HURONIAN ROCKS IN
CENTRAL NORTH CAROLINA.¹

BY H. E. C. NITZE.

The region under discussion embraces a belt, from 8 to 40 miles in width, of metamorphic slates and schists, extending from Virginia in a general southwesterly direction across the central part of North Carolina into South Carolina. This area forms the principal gold ore belt

¹For further discussion of this subject and for map showing the distribution of the rocks here described, see Bulletin 3 N. C. Geological Survey, 1896.



QUEEN POST TRUSS

Floor Plan

Plates kindly loaned by Prof. J. A. Holmes, State Geologist.

American Bank Note Co., N.Y.

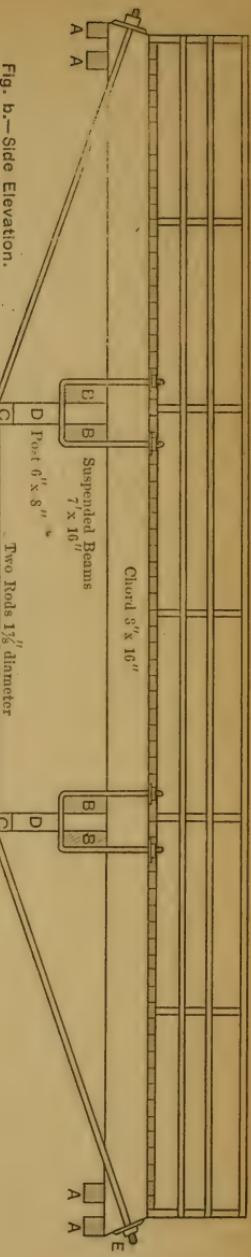
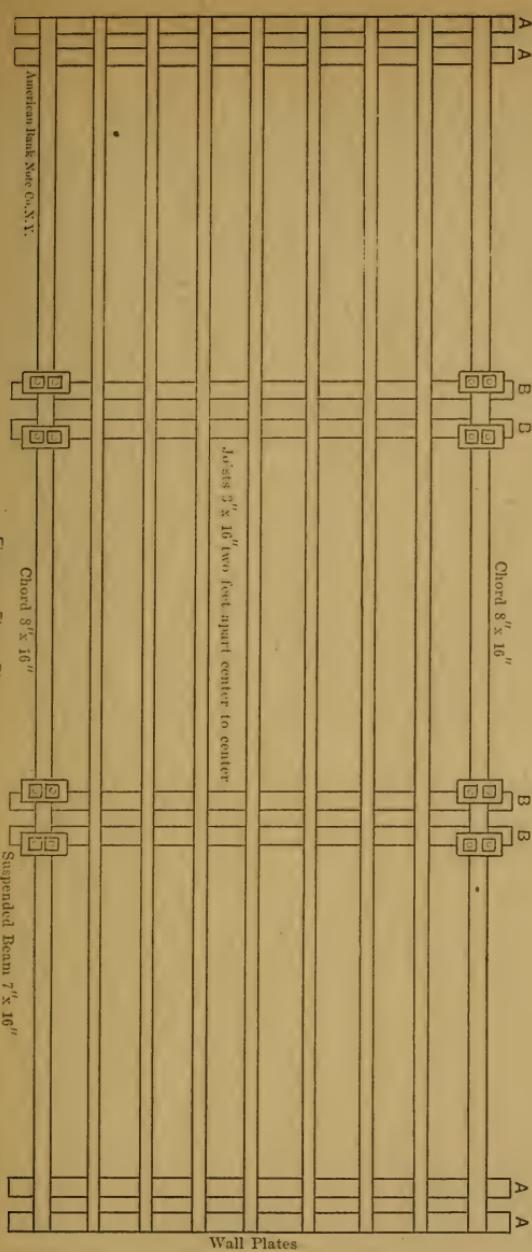


Fig. b.—Side Elevation.

DECK BRIDGE, 45 FEET SPAN.

Side View.



Fig. c.—Cross Section



Fig. d.—Detail of Iron Shoe



Fig. e.—Detail of Iron Washer

of North Carolina, in which connection it is known as the Carolina Slate Belt. It includes, in North Carolina, portions of the counties of Granville, Person, Durham, Orange, Alamance, Chatham, Randolph, Davidson, Rowan, Moore, Montgomery, Stanly, Cabarrus, Anson, and Union. On the west it is bounded by an area of igneous crystalline rocks, and on the east, for the greater part, by the Jura-Trias sandstones, conglomerates and shales.

The general term *slates and schists*, used above, covers a broad designation. The country rocks of the region are:—1) Argillaceous, sericitic (hydro-micaceous), and chloritic slates and schists, all of them more or less metamorphosed. 2) Sedimentary pre-Jura-Trias slates. 3) Ancient volcanic rhyolites, quartz-porphyrries, etc., and pyroclastic breccias, often sheared into a schistose structure. The general strike of the schistosity is N. 20° to 50° E., and the dip is steeply to the northwest.

In 1856, Prof. Ebenezer Emmons, in his *Geological Report of the Midland Counties of North Carolina* (pp. 38-73) described this region and referred the rocks to the Taconic system; and in 1875, Prof. W. C. Kerr, in his *Report of the Geological Survey of North Carolina* (vol. 1; pp. 131-139) included the same rocks in the Huronian.

In order to gain a more comprehensive oversight of this important geological area, it will be well to first state briefly both Emmons' and Kerr's conceptions of their Taconic and Huronian in this part of North Carolina; and then to discuss the same in the light of more recent investigations, carried on by the writer during the latter part of 1894, for the North Carolina Geological Survey. These investigations were unfortunately of a cursory and incomplete nature, and can but form the beginning of a more thorough study of the region later on. However, they will well serve the present purpose of showing the errors into which Emmons and Kerr had fallen, and the miscon-

ceptions they entertained regarding the nature of these rocks, due perhaps chiefly to the lack of petrographic evidences, the science of microscopic petrography being totally unknown in Emmons' days, and certainly in its infancy at the time of Kerr.

EMMONS' TACONIC SYSTEM IN NORTH CAROLINA.

Emmons placed these rocks among the oldest sedimentaries, i. e. at the base of the Paleozoic. In his words:¹ "The formation of the midland counties, which occupy the largest extent of surface, are slates and siliceous rocks, which have been called quartzites." * * * * * "The slates are variable in color and composition. They are mineralogically clay, chloritic, and talcose slates, taking silica into their composition at times, and even passing into fine grits and hornstones, but still variable in coarseness. In the order in which they lie the talcose slates and quartzites are the inferior rocks, though quartzites occur also in the condition of chert, flint or hornstone in all the series."

He established their sedimentary origin from the occurrence of numerous beds containing, in his belief, rounded pebbles. Further, "I found, however, many beds among them which looked like sediments, were porphyritized and somewhat changed, though not strictly porphyries. I found after much search too, beds which were unequivocally pebbly; and finally, to remove all doubt, I was fortunate in discovering that the porphorized beds also frequently contained pebbles; proving most conclusively that they are sediments which were partially altered."²

One of the arguments that Emmons used to prove the sedimentary nature of the Taconic, and its derivation from the basal complex, is the presence of gold in the

¹ Geol. Report of Midland Countiss of N. C.

² Ibid, p. 47.

slates and schists, "which of course must have been commingled with the sediments at the time these rocks were deposited." * * * * "The gold exists mostly in the western belt of granite in the veins belonging to the hornblende and gneiss of the Blue Ridge."

Furthermore he claimed to have discovered in his Lower Taconic sandstones and cherty beds at Troy and Zion (12 miles southwest of Troy) in Montgomery county, several species of fossils.² He described these as siliceous corals of a lenticular form, from the size of a pea to two inches in diameter. Two varieties are distinguished and named by him: *Paleotrochis* (old messenger) major and, *Paleotrochis* minor. The following descriptive section, in the ascending order of the rocks and beds, in which these supposed fossils were found, is given:

"(1) Talcose slates, passing into siliceous slates, and which are often obscurely brecciated. Thickness undetermined.

"(2) Brecciated conglomerates, sometimes porphyritized.

"(3) Slaty breccia, associated with hornstone.

(4) Granular quartz, sometimes vitreous and filled with fossils and siliceous concretions of the size of almonds; two to three hundred feet thick.

"(5) Slaty quartzite with very few fossils; about fifty feet thick.

"(6) Slate without fossils; forty feet thick.

"(7) White quartz, more or less vitrified, filled with fossils and concretions; seven to eight hundred feet thick.

"(8) Jointed granular quartz, with only a few fossils.

"(9) Vitrified quartz without fossils, and thickness very great, but not determined,

"The fossils also occur in the variety of quartz or quartzite known as burrystone, and which is often porphyritized."

¹Ibid, p. 57.

²Ibid pp. 48. 60.

These fossiliferous beds are stated to be sometimes auriferous.

He is therefore disposed from the above facts, to place all of the rocks not decidedly igneous, that is, those which he regarded as stratified (though in reality the apparent stratification is but schistose lamination), with the sediments. He then correlates these rocks with the taconic, the infra-silurian sediments of Massachusetts, based mainly on "their lithological characters, and the relations in which they are placed to the older rocks, and those which they sustain to each other." In North Carolina, he says, these rocks have been derived from syenitic granites, which he believes to belong to the primary or basal complex. He makes two divisions, the Lower Taconic and the Upper Taconic, noting that the distinction between them, however, is less obvious in North Carolina than in the northern equivalents.

The Lower Taconic, "The Lower series will contain the talcose slates, white and brown sandstone, or quartz, which is frequently vitrified or cherty, and the granular limestone and associated slates."¹

The talcose slates are stated to be made up of talc and fine grains of quartz, becoming a friable sandstone when quartz predominates. Color and lustre silvery when chlorite is absent, and greenish when chlorite is present. The following varieties of these quartz rocks are given:²

- "(1) A fine grained coherent quartz.
- "(2) A fine grained friable quartz.
- "(3) A fine grained micaceous and talcose quartz.
- "(4) Vitrified quartz or chert. (a) green, blue, (b) agatized.
- "(5) A cherty or apparently porphyritized quartz, which contains feldspar, which decomposes and leaves a rough porous mass similar to burrstone.

¹ Ibid, p. 49; Ibid, p. 51

² Ibid, p. 55.

“(6) Pebbly and semi-brecciated quartz.

“(7) Common brown quartz.”

This rock * * * * is associated with * * * talcose slates. It is repeated two or three times. * * * It frequently contains beds of pebbles. But its most interesting feature appears in its passage into hornstone, chert or flint.”

The apparent vitrification he considers due to a chemical combination of the particles, that is, to a cause independent and distinct from heat.

“Agalmatolite” (pyrophyllite) is mentioned as occurring in beds in this Lower Taconic series. And limestone, containing talc and tremolite, is said to be associated with slate and quartz,

Emmons’ rocks of the Lower Taconic, then are:¹

(1) “Beds of talcose slates. (2) Quartz rocks with their alternating series of talcose slates. (3) Beds of agalmatolite. (4) Limestone with its interlaminated slates.

The Upper Taconic. “This division of the system is not very clearly marked. * * * In North Carolina the line of demarcation is sometimes difficult to define. But the rocks which I regard at the present time are (in ascending order):

(1) “Argillaceous, or clay slates, with many subordinate beds; roofing slates, mountain slate.

(2) “Chloritic and argillaceous sandstones, flagging stones, etc. .

(3) “Brecciated conglomerates.

The ordinary soft, greenish slates may be regarded as the prevailing mass of the first division. The predominant color is greenish gray. A red decomposed variety is mentioned as being common near Pittsboro, Chatham county. “The subordinate beds are fine siliceous ones passing into chert or hornstone. * * * * The colors are blue, purple and green.”

¹ Ibid, p. 55.

² Ibid p. 65.

"The slate in the ascending order is more and more interlaminated with thick beds, which have an intermediate composition between a sandstone and slate, the second division. * * * Among them are beds of conglomerate. These beds may be mistaken for trap, being greenish and tough, and besides like trap the broken strata become concretionary and exfoliate in concentric layers."

"The brecciated conglomerate has an argillaceous or chloritic base. The mass is composed in the main of fragments of other rocks mostly retaining an angular form. The fragments are sometimes eighteen inches, and even two feet long."

"The clay slates and breccia, with their intermediate beds are traversed by veins of milky quartz. They are sometimes auriferous."

The so-called quartzite of both the Upper and Lower Taconic is considered of such peculiarity that a separate chapter is devoted to its description. It is described as an uncristallized quartz, resembling gun-flint, and is also called flint, chert and hornstone. Color bluish-black, passing to purple, grayish, white and green; sometimes banded; texture fine when compared with the finest sandstone; translucent on edges; fracture flat conchoidal; often porphyritic, porphyritized; and it is stated that frequently the fresh fracture is dotted with small limpid crystals of quartz.

"The varieties of quartzite are numerous if color and texture are made grounds of distinction:¹

- (1) "Light gray and compact, or very finely granular.
- (2) "Smoke gray, with grains of hyaline quartz disseminated in the mass.
- (3) "Texture fine granular, with drab color.
- (4) "Porphyritized quartzite.
- (5) "Light green quartzite.

¹ Ibid, p. 71.

(6) "Greenish, and full of cavities, and frequently epidemic.

(7) "Banded quartzite, or coarsely agatized.

"These forms of quartzite are not confined to rocks of a particular age, or to a given series. They seem to be distributed through formations of all ages and epochs. They are common to both divisions of the Taconic."

Emmons explains their origin from an aqueous chemical standpoint.¹

KERR'S HURONIAN SYSTEM IN CENTRAL NORTH CAROLINA.

Kerr recognized five principal outcrops of the Huronian rocks. The one that corresponds to the Central Slate belt, and hence of interest here, is stated to lie on the west side of the Raleigh granite.² "The bottom beds are argillaceous and talcoid.* * * Three or four miles from Raleigh these slates become highly plumbaginous, * * * and a heavy body of micaceous, white, slaty quartzites follows closely along the west side of the graphite.

Alternations of argillaceous, talcoid and quartzitic beds continue for five or six miles, when they disappear beneath a narrow trough of Triassic sandstones, beyond which they emerge along an irregular, but approximately northeast and southwest, line in the central mineral bearing slate belt. * * * This tract extends quite across the State in a breadth of 20 to 40 miles, and is composed of siliceous slates and clay slates chiefly; the former being often brecciated and conglomerate, the pebbles sometimes a foot and upwards in diameter, frequently chloritic, and often passing into hornstone and chert, and occasionally into quartzite. The clay slates are generally thin-bedded, often shaly, gray, drab, banded, blue and frequently greenish from an admixture of chlorite; sometimes tal-

¹Ibid. pp. 51 and 72.

²Report of the Geol. Sur. of N. C., 1875, Vol. 1. pp. 181-9.

coid or hydro-micaceous; and very often they may be better described as conglomerate slates, being composed of flattened and differently colored soft, slaty fragments of all sizes, from minute particles to an inch and more in diameter. * * * * * In Montgomery county, in a very heavy ledge of siliceous slates, occurs a siliceous conglomerate, which is filled for hundreds of feet with very singular siliceous concretions, some of which Dr. Emmons has described under the name of *Paleotrochis*; but the rock for several miles, as well as at this particular locality, contains a multitude of rounded and ovoid masses from the smallest sizes to that of a hen's egg: showing the wide prevalence of conditions favorable to the operation of concretionary forces. * * * The talcose, siliceous, chloritic slates are more abundant towards the base of the series, the east side, and the clay slates predominate on the west."

He also mentions the occurrence of beds of pyrophyllite, and the abundance of quartz veins. The strike is given as northeast, and the dip prevalently west at steep angles.

"The belt is bounded on both sides by the Laurentian, on which it lies unconformably, and from which its materials were derived. The stratigraphy therefore indicates the horizon of these rocks to be the Huronian, and lithology agrees with that determination."¹

RESULTS OF MORE RECENT PETROGRAPHIC STUDIES.

The Slates and Schists. One of the results of the late geological work in this belt has been to identify at least the argillaceous, sericitic, and chloric schists and slates with those of Emmons' Taconic and Kerr's Huronian. These rocks are termed schists, and again they are termed slates. Certainly a great number of them have a true slaty cleavage, while others are more truly schistose, i. e. the laminae are not essentially parallel. These different

¹ *Ibid.*, p. 133.

structural effects are due to dynamo-metamorphic action on materials of different composition. The argillaceous types might more properly be called the slates (clay-slate, thon-schiefer, argyllite, phyllite) as they contain more uncrystalline matter, and possess a more definitely slaty structure. So also bedding planes are more easily distinguishable in these, if at all; and altogether their sedimentary or clastic origin is more evident. At the same time they are metamorphosed in varying degrees, and possess many secondary cleavage structures. These slates often have a calcareous tendency in their composition, as is exemplified by the numerous small calcite seams that intersect them, and the coatings of calcite on their cleavage planes.

The term *talc* (*talcose*, *talcoid*) slate or schist, used by Emmons and Kerr, and generally by many others, is a mistaken one. It is true that it is perhaps an excusable error, for these slates and schists are often so soft and greasy that the resemblance to talc is very great. However, chemical analysis and other characteristics would place the mineral in the class of hydro-muscovite or sericite, the percentage of magnesia being far too small for talc. Several analyses of type specimens of this rock from the Haile gold mine in Lancaster county, S. C., by Dr. Chas. Baskerville, of the University of North Carolina, show:

SiO_2	44.61	61.02
Al_2O_3	31.57	25.54
FeO	3.55	4.46
CaO	0.20	0.60
MgO	0.22	0.14
MnO	0.16
Na_2O	6.96	2.19
K_2O	6.97	1.81
H_2O	5.80	4.20
	100.04	99.96

The term that I shall therefore use as more appropri-

ate is sericite schist. The true talc schists are very rare.

The chloritic schists are probably more truly crystalline schists, and are richer in accessory metamorphic minerals, such as garnet and epidote.

The argillaceous slates and sericite schists are frequently silicified; the chlorite schists are not as a rule. This silicification exists in varying degrees up to a completeness which renders the rock so hard that it resists scratching with a knife.

The strike of the formation as a whole is generally northeast, and the dip steeply to the northwest. These strikes and dips refer to the schistosity of the rocks, and not to the bedding planes.

In general the force producing schistosity and slaty cleavage appears to have acted downward from the northwest, producing normal faulting with but little deformation. No instance of reverse faulting was recorded.

Now, as to the origin of these schistose and slaty rocks; in part it seems that they must be sedimentaries altered by dynamo- and hydro-metamorphism. The evidence of this is offered by several observations of bedding and banding extending across the schistosity, generally at low angles, although in most instances this original structure has been obliterated. Emmons' supposition that the gold in the slates and schists is of sedimentary origin (page 55) is altogether untenable.

The lamination or schistosity, however, is wholly the effect of shearing, produced by dynamo-metamorphism. It has no connection with bedding planes of stratigraphic structure, as both Emmons and Kerr supposed. The original bedding planes may correspond to certain of the present cleavage planes, i. e. lie parallel to them, but in that case the bedding structure has been obliterated. Schistosity must not be confounded with bedding.

It does not seem probable, at the present stage of investigation, that these slates have been derived from the granitic and other more basic igneous masses lying on

the west; for these are supposed to be later intrusive bosses.

That others of these schists, particularly the chloritic varieties, are metamorphosed, sheared eruptives seems most probable. They are even porphyritic and brecciated in places. In fact Emmons hints at such rocks in his description of his Upper Taconic chloritic member, when he says: "These beds may be mistaken for trap, being greenish and tough, and besides like trap, the broken strata become concretionary and exfoliate in concentric layers." (Page 59.) This subject will be recurred to later on.

The Monroe Slates. At Monroe, in Union county, a considerable area of truly bedded and but little indurated or metamorphosed slates was discovered. Similar slates were also found at the Parker gold mine near New London, Stanly county, at the town of Albemarle in Stanly county, and at the Sam Christian gold mine in Montgomery county. Thus they presumably cover a large area in the southeastern portion of the Carolina Slate Belt. In the fresh condition this slate is black, weathering to dark and light drab, greenish and even reddish colors. At the railroad station (Monroe) it lies in a low, gently undulating anticlinorium. Several hundred yards south of the depot the strike is N.85°E., and the dip is 30°S.E. At a point $\frac{1}{4}$ mile north of the depot it is finely banded and lies nearly horizontal. It has been quarried here for use as paving blocks in Monroe.

That these slates are of sedimentary origin and of later age than the slates and schists to the west and north can scarcely admit of doubt. They are reported to dip under the Jura-Trias conglomerate at Polkton, about 20 miles east of Monroe, and might be looked upon as Lower Palaeozoic; but the absence of fossils (at least so far none have been found, though a careful search is certainly warranted) must, for the time being, place them provis-

ionally in the Algonkian. They might appropriately be named the *Monroe* slates.

The Volcanic Series. The middle member of Emmons' Lower Taconic is the quartz rock (white and brown sandstone), which is stated by him to exist in many varieties; (p. 57). I did not observe any true granular quartzites, such as characterize the Cambrian for instance (even in a metamorphosed state); and in fact, from Emmons' and Kerr's descriptions, their rocks of this class are rather fine-grained, thin bedded, quartzose schists, and devitrified quartz or chert, often porphyritized and brecciated. It is probable that Emmons' fine grained talcose quartz (p. 58) corresponds to the silicified schists, (p. 63) whose quartzitic nature is due to a later hydro-silicification.

The crypto-crystalline varieties of quartz (flint, chert, hornstone) are of especial interest, and warrant a careful consideration. It is at present the opinion that these rocks belong to the class of ancient (pre-Cambrian) acid volcanics, in many respects analogous to, and probably contemporaneous with, similar rocks of the South Mountain in Maryland and Pennsylvania, whose discovery was first announced by the late Dr. George H. Williams.¹ Miss Florence Bascom has described the origin, devitrification and structure of the acid types of these rocks.² And Dr. Williams has outlined the general distribution of the ancient volcanic rocks along the eastern border of North America.³ These rocks are analogous also to the halleflintas and eurites of Southern Sweden, described as volcanic rocks by Nordenskjöld. They would also correspond to Hunt's pre-Cambrian petro-silex rocks, called by him the Arvonian, being below his Huronian.

The hornstones have every appearance of being acid feldspar quartz rocks, and will probably be found, on

¹ The Volcanic Rocks of the South Mountain in Pa. and Md. Am. Jour. Sci. xliv., Dec. 1892. pp. 482—496.

² Jour. Geology, Vol. 1. 1893. pp. 813—832.

³ Jour. Geology, Vol. 2. 1894. pp. 1—31.

further study, to belong to the class of apo-rhyolites, a term introduced by Miss Bascom to denote a devitrified rhyolite. Emmons describes the type very well under the head of quartzite (p. 59). They resemble perfectly crypto-crystalline quartz, and on weathering present an earthy, yellowish surface. The color of the fresh rock is drab, bluish to almost black; translucent on edges; fracture flat conchoidal; sometimes banded, showing flow structure, as at the Silver Valley mine in Davidson county, where the rock is locally called "gun-flint." It often contains small crystals of metallic sulphurets, chiefly pyrite with some galena, chalcopyrite and blende.

At the Moratock gold mine in Montgomery county, a siliceous rock occurs in large masses, which at first sight resembles a compact, homogeneous hornstone, but which on close investigation is found to be dotted with small, dark-colored, glassy specks. These are minute quartz crystals, and the microscopic examination of thin sections shows the rock to be an undoubted quartz-porphyry. Its true porphyritic character is best illustrated in the weathered specimens, the feldspathic groundmass being decomposed and altered, leaving the quartz phenocrysts clearly outlined. The flow structure is also beautifully brought out in the weathered groundmass.

Emmons, in his description of his quartzite, states that it is often porphyritic and porphyritized, and that frequently the fresh fracture is dotted with small limpid crystals of quartz (p. 59).

In the enumeration of the varieties of Lower Taconic quartz rocks (p. 57) he mentions a cheety or apparently porphyritized quartz, which contains feldspar, which decomposes and leaves a rough porous mass similar to burrstone." Kerr says: "In Montgomery county, in a very heavy ledge of siliceous slate, occurs a siliceous conglomerate which is filled for hundreds of feet with very singular, siliceous concretions, some of which Dr. Emmons has described under the name of *Paleotrochis*;

but the rock for several miles, as well as at this particular locality, contains a multitude of rounded and ovoid masses, from the smallest sizes to that of a hen's egg, showing the wide prevalence of conditions favorable to the operation of concretionary forces" (p. 61). These gentlemen have without much doubt described the quartz porphyry of the Moratock mine, or one similar thereto.

It appears highly probable that at least some of these siliceous, so-called pebbly concretions are spherulites. Whether they constitute Emmons' pebbly beds, from which he determined the sedimentary origin of his Taconic, is not known. However, it is quite possible that they misled him in that direction. Certain it is that he says: "I found, however, many beds among them (slates and associated rocks) which looked like sediments, were porphyritized, and somewhat changed, though not strictly porphyries. I found after much search too, beds which were unequivocally pebbly; and finally, to remove all doubt, I was fortunate in discovering that the porphyritized beds also frequently contained pebbles; proving most conclusively that they are sediments which were partially altered" (p. 55).

Thus he evidently mistook either the concretionary form of the weathered porphyry and felsite, or else the partially rounded felsite fragments in the accompanying pyroclastic breccias (which will be spoken of later on) for pebbles.

¹Prof. Marsh in 1867 made a short study of Emmons' Paleotrochis, and in his words: "An examination of the interior of several specimens clearly indicated that they were not corals, and as soon as microscopical specimens could be prepared, they were more carefully examined, but no trace of organic structure could be detected, the entire mass being evidently a fine grained quartz. The specimens examined were undoubtedly authentic examples

¹ Am. Jour. Sci. (2), Vol. 45, 1868, p. 217.

of *Paleotrochis*, as some of them presented to the Yale cabinet by Prof. Dana, were sent to him by Prof. Emmons, and the rest were given to the writer by Prof. W. C. Kerr, the present state geologist of North Carolina. * * * * Admitting the inorganic nature of these remarkable forms, their origin becomes an interesting question, and it certainly is not easy to give a satisfactory explanation of it. They appear, however, to have some analogy with "cone in cone," which, as the writer has shown elsewhere,¹ is probably due to the action of pressure on concretionary structure when forming. In some respects the two are quite distinct, but evidence of pressure is clearly to be seen in both."

Kerr evidently agreed with Marsh as to the inorganic nature of the *Paleotrochis*, and Mr. C. D. Walcott, the director of the U. S. Geological Survey, entertains the same opinion.²

According to both Emmons' and Kerr's descriptions, these peculiar forms appear to occur in what are now known to be the acid effusive rocks. In his descriptive section of the rocks which carry the *Paleotrochis*, Emmons names the following (p. 56):

"Granular quartz, sometimes vitreous and filled with fossils and siliceous concretions of the size of almonds.

"Slaty quartzite with very few fossils.

"Slate without fossils.

"White quartz more or less vitrified filled with fossils and concretions.

"Jointed granular quartz with only a few fossils."

And he says: "These fossils also occur in the variety of quartz or quartzite, which I have described as burrystone, and which is often porphyritized." (p. 56.)

An interesting point is suggested in the above succession of rocks, namely, that there was more than one vol-

¹ Proc. Amer. Assoc. Adv. Sci., vol. 16, 1867, p. 135.

² Private communication to the writer.

canic outbreak, and during at least one period of inactivity sedimentary slates (the Monroe slates) were deposited.

These acid volcanics are accompanied by pyroclastic breccias and basic eruptives. The basic rocks are of dark green color, and are perhaps pyroxenic in composition. They cover large areas, and are often massive or only partly schistose; again they are largely sheared into schists. It is quite probable that most of the *chloritic* schists in this part of the Carolina Slate Belt are of this nature.

The breccias consist of this basic material in which are imbedded angular fragments of the felsite (apo-rhyolite) or porphyry up to one foot in diameter. They are distinctly pyroclastic breccias and hence the basic rock, or porphyrite as it may be provisionally called, is later than the quartz porphyries and rhyolites. This would agree with the generally accepted law of eruptions, i. e. from the normal to the acid to the basic types.

Emmons, in his description of the Upper Taconic, mentions brecciated conglomerates as the most remarkable mass of this division. As he states, "It has an argillaceous or chloritic base. The mass is composed in the main of fragments of other rocks, mostly retaining an angular form; but frequently rounded and worn rocks are enclosed in the mass. The fragments are sometimes 18 inches and even 2 feet long." (p. 59.)

Kerr mentions brecciated and conglomerated (siliceous) slates, the pebbles sometimes a foot and upwards in diameter, frequently chloritic and often passing into hornstone and chert, and occasionally into quartzite" [p. 60]. That these rocks correspond to the above described pyroclastic breccias is at once evident.

These ancient volcanics have also been found covering large areas in Chatham and Orange counties, near the eastern edge of the Carolina Slate Belt, and fully 40 miles east of the region including the above described

localities. During the summer of 1893, Dr. George H. Williams in company with Prof. J. A. Holmes, State Geologist of North Carolina, made a reconnaissance trip through Chatham and Orange counties, the results of which are included in Dr. Williams' paper on the distribution of the ancient volcanic rocks in eastern North America.¹ He says: "In a drive from Sanford to Chapel Hill an abundance of the most typical ancient lavas, mostly of the acid type, was encountered. On the road from Sanford to Pittsboro purple felsites and porphyries showing spherulitic and beautiful flow structures, and accompanied by pyroclastic breccias and tuffs, were met with two miles north of Deep river, and were almost continuously exposed on Rocky river. Here devitrified acid glasses with chains of spherulitic and eutaxitic structure were collected, while beyond, as far as Bynum on Haw river, four miles northeast of Pittsboro, the only rocks seen were of the same general character. On the farm of Spence Taylor, Esq., in Pittsboro, a bright red porphyry with flow lines is exposed in so altered a condition that it can easily be cut into any form with a knife, though it still preserves all the details of its structure. * * *

Three-quarters of a mile beyond Pittsboro, on the Bynum road, there is a considerable exposure of a basic amygdaloid. South of Hackney's Cross Roads there are other excellent exposures of ancient rhyolite with finely developed spherulitic and flow structures. * * * Another locality in the volcanic belt was visited on Morgan's run, about two miles south of Chapel Hill. Here are to be seen admirable exposures of volcanic flow and breccias with finer tuff deposits, which have been extensively sheared into slates by dynamic agency. Towards the east and north these rocks pass under the transgression of Newark sandstone. * * * From still another locality at the Cross Roads near the northern boundary of

Chatham county, fifteen miles southwest of Chapel Hill, Professor Holmes informs me that specimens of undoubted volcanic rocks have recently been secured. He has also sent me, within the past month, a suite of similar specimens from Pace's Bridge, on Haw River, three miles above Bynum."

Since that time the same volcanics have been found at the Narrows of the Yadkin river, along the Deep river at Lockville, and for five or six miles northwest of Lockville. At the last two localities the masses are often brecciated and usually sheared into perfect crystalline chloritic schists.

It is of interest to note, in the above descriptions of Dr. Williams, the occurrence, on the Taylor farm near Pittsboro, of a bright red porphyry with flow lines, in so altered a condition that it can be easily cut into any form with a knife. This is undoubtedly the same rock, and from the same locality, as that described by Emmons as a decomposed red variety of his Upper Taconic argillaceous or clay slate. (p. 58).

Conclusions. In this brief resumé, then, we can recognize Emmons' Taconic and Kerr's Huronian rocks of the central gold-bearing slate belt.

The bitter controversies regarding the Taconic question among geologists are well known, and need not be taken up here. It is sufficient to say that geologists by later and more detailed work and study have seen fit to differentiate various members of the old Taconic system in different parts of the country, and refer them to more definite horizons. Thus the granular quartz of Emmons' typical Taconic section in the Berkshire Hills of Massachusetts, has been found to be characterized by the *Olenellus* fauna of the Lower Cambrian; and the Berkshire or Stockbridge limestone by the Chazy-Trenton, and perhaps at its base by an Upper Cambrian fauna; and the original Lower Taconic slate of Emmons is correlated, by its stratigraphic position, with the Hudson

shales.¹ In 1888, Walcott, in studying a section of these rocks in Newfoundland, placed, from paleontological evidences, the "Red Sandrock" series, the Georgia shale and slate series, the "Granular Quartz" and "the Upper Taconic" of Emmons beneath the Middle Cambrian or Paradoxides zone of the Atlantic coast.²

And so the rocks of the old Taconic or Huronian belt in central North Carolina must also in time be differentiated and recorrelated when they have been more carefully studied.

Emmons was in a measure quite correct in calling his Taconic rocks of central North Carolina the bottom sediments, and placing them below the Silurian. The absence of fossils in the slates, however, necessitates our going back still another step, and placing them below the Cambrian sediments, in the Algonkian, which Van Hise has defined as including all recognizable pre-Cambrian clastics and their equivalent crystallines, the base of the Cambrian being placed at the *Olenellus* fauna.³ Here the matter must rest until we can find fossils in the rocks, or verify the organic character of Emmons, *Paleotrochis*; or until we can trace the rocks into a terrane of known age. So also the pyroclastic volcanics must be looked upon as pre-Cambrian.

It is of interest to note that here, as in other portions of eastern North America, the ancient volcanics occur in close proximity to the western edge of the Jura-Trias basin. Adopting Suess' theory of the formation of moun-tians, we may look upon this central belt of sheared and faulted slates as the levelled site of an ancient Atlantic mountain range; while the bordering Jura-Trias represents a transgression formed by the sunken block on the east; and the early phases of this subsidence were accompanied by the exhibition of volcanic forces.

¹ U. S. Geological Survey. Bull. 81. Correlation Papers: by C. D. Walcott; 1891, p. 243.

² *Ibid.* p. 113.

³ U. S. Geological Survey. Bull. 86. Correlation Papers: Archean-Algonkian; p. 495.

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